

Alma Mater Studiorum – Università di Bologna

**DOTTORATO DI RICERCA IN
CHIMICA**

Ciclo 29°

Settore Concorsuale di afferenza: 03/B1

Settore Scientifico disciplinare: CHIM/03

**INNOVATIVE GEOPOLYMERS BASED ON
METAKAOLIN:
SYNTHESES AND APPLICATIONS**

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Esame finale anno 2017

Itaca

*“Quando partirai, diretto a Itaca,
che il tuo viaggio sia lungo
ricco di avventure e di conoscenza.
Non temere i Lestrigoni e i Ciclopi
né il furioso Poseidone;
durante il cammino non li incontrerai
se il pensiero sarà elevato, se l'emozione
non abbandonerà mai il tuo corpo e il tuo spirito.
I Lestrigoni e i Ciclopi e il furioso Poseidone
non saranno sul tuo cammino
se non li porterai con te nell'anima,
se la tua anima non li porrà davanti ai tuoi passi.
Spero che la tua strada sia lunga.
Che siano molte le mattine d'estate,
che il piacere di vedere i primi porti
ti arrechi una gioia mai provata.
Cerca di visitare gli empori della Fenicia
e raccogli ciò che v'è di meglio.
Vai alle città dell'Egitto,
apprendi da un popolo che
ha tanto da insegnare.
Non perdere di vista Itaca,
poichè giungervi è il tuo destino.
Ma non affrettare i tuoi passi;
è meglio che il viaggio duri molti anni
e la tua nave getti l'ancora sull'isola
quando ti sarai arricchito
di ciò che hai conosciuto nel cammino.
Non aspettarti che Itaca ti dia altre ricchezze.
Itaca ti ha già dato un bel viaggio;
senza Itaca, tu non saresti mai partito.
Essa ti ha già dato tutto, e null'altro può darti.
Se, infine, troverai che Itaca è povera,
non pensare che ti abbia ingannato.
Perché sei divenuto saggio, hai vissuto una
vita intensa,
e questo è il significato di Itaca.”*

Ithaka

“As you set out for Ithaka
hope the voyage is a long one,
full of adventure, full of discovery.
Laistrygonians and Cyclops,
angry Poseidon don't be afraid of them:
you'll never find things like that on your way
as long as you keep your thoughts raised high,
as long as a rare excitement
stirs your spirit and your body.
Laistrygonians and Cyclops,
wild Poseidon you won't encounter them
unless you bring them along inside your soul,
unless your soul sets them up in front of you.
Hope the voyage is a long one.
May there be many a summer morning when,
with what pleasure, what joy,
you come into harbors seen for the first time;
may you stop at Phoenician trading stations
to buy fine things,
mother of pearl and coral, amber and ebony,
sensual perfume of every kind
as many sensual perfumes as you can;
and may you visit many Egyptian cities
to gather stores of knowledge from their scholars.
Keep Ithaka always in your mind.
Arriving there is what you are destined for.
But do not hurry the journey at all.
Better if it lasts for years,
so you are old by the time you reach the island,
wealthy with all you have gained on the way,
not expecting Ithaka to make you rich.
Ithaka gave you the marvelous journey.
Without her you would not have set out.
She has nothing left to give you now.
And if you find her poor, Ithaka won't have
fooled you.
Wise as you will have become, so full of
experience, you will have understood by then
what these Ithakas mean”.

Konstandinos Kavafis

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Chapter 1

Introduction and finalities

1.1

History and theory

Since the early 30's some scientists, including Khul (1930), Chassevent (1940) and Glukhovsky (1957) experimented the behavior of some aluminosilicate materials from industrial waste mixed with sodium and potassium hydroxide solutions in order to obtain special cements "clinker-free" [1].

The turning point in the study of these materials occurred in 1979 when Joseph Davidovits published the first notice of geopolymers. Later he patented the binder obtained by mixing metakaolin and alkaline solutions under various commercial names such as Geopolymite and Pyrament; the first one is a real geopolymeric mineral resin based on metakaolin, the second is a material very similar to a pozzolanic cement formed by 80% Portland and 20% geopolymeric component.

Davidovits is considered the inventor of the geopolymer because he was the first to describe the concept of geopolymerization, the reactions involved, the nomenclature and the possible resulting structures as a function of Si/Al ratios [2].

He highlighted with the "geo" suffix some intrinsic characteristics of these material that simulate, for chemical composition and mineralogical structure, natural compounds as zeolite, can exhibit basic properties as hardness, chemical stability and long-life similar to that geological [3].

Geopolymers belong to so-called "Low-Calcium alkali-activated binders". Today these term is generically used to describe an amorphous alkali aluminosilicate which is also commonly known as "Inorganic polymer", "Alkali activated cement", "Geocement", "Alkali-bonded ceramic", "Hydroceramic", etc.....

Despite this variety of nomenclatures, all these terms describe materials synthesized utilizing the same chemical process which can be described as a complex system of dissolution and precipitation reactions in an aqueous alkaline solution.

Thus in other terms, a geopolymer is an artificial material obtained by the chemical reaction between reactive aluminosilicate raw materials and alkaline activators.

This reaction, called geosynthesis or geopolymerization, is a polycondensation reaction, similar to those of some organic polymers and takes place at room temperature.

The result is the formation of a disordered alkali aluminosilicate gel phase, known as *geopolymer gel binder* [6].

Figure 1 [4] shows the main differences between the “Low-Calcium alkali-activated system” and the “High-Calcium alkali-activated system”. This distinction is drawn on the basis of the calcium content which derives mainly from aluminosilicate powder.

In the first system (the right-hand pathway), these gel types is often represented as N-A-S-(H), where N is the Sodium (Na) and H is the water. In this case H is shown in parentheses to indicate that the water is not a structural component of this gel, as it is in C-A-S-H-type [5] but is only a “reaction medium”, that does not take part in the formation of the gel and is released during the polymerization process (only in theoretical terms).

Due to the complexity of these materials (figure 1) caused by the enormous compositional variety, this PhD thesis is focused on geopolymer (N-A-S-(H) type formulations. Thus in this introduction will be strictly presented general characteristics of geopolymer while in the following chapters, will be considered only the specific class of geopolymer based-on metakaolin.

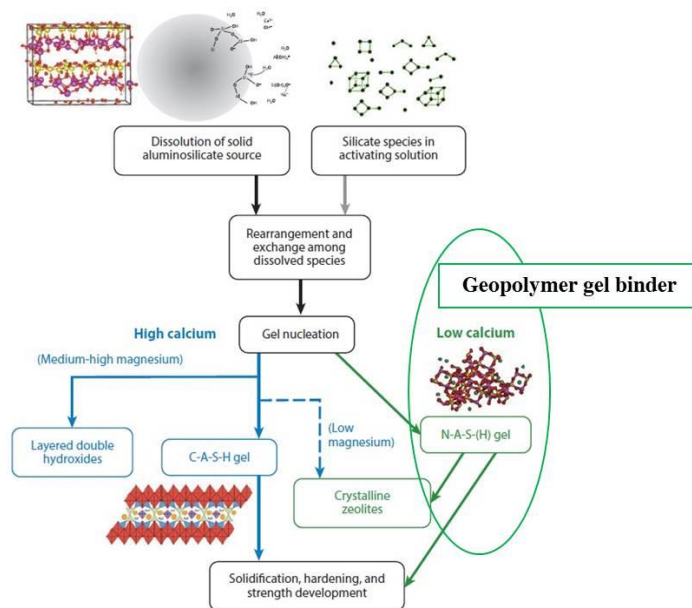
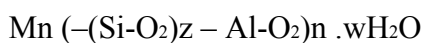


Figure 1- Process and reaction products of alkaline activation of a solid aluminosilicate precursor. High-calcium systems react according to the left-hand pathway, whereas low-calcium systems react according to the right-hand pathway [4].

1.1.1 Geopolymeric structure

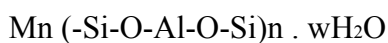
Geopolymers are considered formed by a short orderly molecular network within SiO_4 and AlO_4 tetrahedra linked by oxygen bridges [6]. In this configuration, the AlO_4 tetrahedron introduces a negative charge, which the alkali metal balances. The sequence of the SiO_4 and AlO_4 tetrahedra is considered influenced by the Lowenstein Avoidance Principle [7]: an AlO_4 tetrahedron cannot be directly linked to a second AlO_4 tetrahedron; they require a SiO_4 tetrahedron bridge. In principle, almost any positive ion could be used to act as the charge-balancing ion.

Geopolymers can be described by the empirical formula:



where: $Z = 1, 2 \text{ o } 3$; $M = \text{Na}^+ \text{ o } \text{K}^+$; $n = \text{degree of polymerization}$

For example, if $Z = 2$, the polysialate (Davidovits' nomenclature) will present the following formula:



and will be named poly (sialate-siloxo) [8].

Geopolymer gels are characterized by three-dimensional structures that vary significantly depending on the raw materials (aluminosilicate powder, alkaline activator and their ratios), degree of reaction and curing temperature.

Due to these aspects, as mentioned above, is very difficult to use an unique model to describe all these alkali-activated materials. In the scientific literature there are different representations of these through diagrams and pictures (similar to those reported in figure 2) that show a possible geopolymeric nanostructure in which the tetrahedra are linked by oxygen bridges [6].

Thanks to the compact network (and chemical composition) their properties, including high mechanical strength, fire resistance, dimensional stability, acid resistance, excellent adhesion to the aggregates and reinforcements, may be similar, depending on the formulation, to those of conventional materials such as ceramics, zeolites, refractory materials, cement and mortars.

Water is an important component of the formulation because it influences the final porosity of the materials. It is known that the porosity is strongly dependent on the water content in "geopolymeric precursors" but also by the subsequent water elimination process during the reaction mechanism [9].

Porosity determines some characteristics and final applications. In fact, generally, open porosity of binders can vary between 20 to 40%. The pores width is in the range from subnanometre to several tenths of a millimeter [10]. For specific applications, such as to reduce the weight of concrete (low density) or to produce materials for acoustic and thermal insulation, the porosity can be increased until 70-95% by different foaming methods [9,11].

While macrostructural aspects and pore distribution can be quite easily controlled by SEM observations and porosimetric analysis it is much more difficult to verify their nanostructures due to the partial amorphization after geopolymerization.

Probably, the most interesting and accepted models were obtained from studies by MAS-NMR and most recently through advanced *beamline techniques* that provide information about the correlations and distances of atoms or the presence of water or hydroxyl groups into the pores of materials [12].

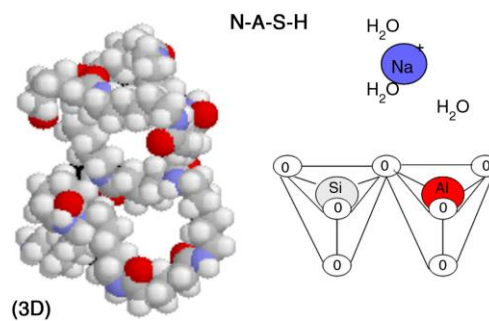


Figure 2- SiO₄ and AlO₄ tetrahedra linked by oxygen bridges

In particular the combination of a variety of beamline-based techniques has been shown to provide detailed nanoscale information regarding the chemistry of alkali-activated binders, which has not been accessible through traditional laboratory analysis.

For example *Synchrotron infrared microscopy* shows the detail of the effects of nanoparticle seeding on geopolymer gel homogeneity at a chemical and microstructural level. *In situ neutron pair distribution function analysis* (PDF) shows the evolution of both bonding environments in framework and non-framework species during the formation of the geopolymer binder. *X-ray fluorescence microscopy* provides an understanding of elemental distributions on a length scale as fine as tens of nanometers, while *X-Ray tomography* provides the opportunity for three-dimensional reconstruction of the distribution of pore and solid phases. Each of these techniques in isolation is powerful, but by combining the data available through *in situ* and *ex situ* analysis and

across a wide range of length scales, a more holistic understanding of the binder structure can be obtained [12].

For example *Infrared* and *X-ray fluorescence microscopy*, and *Nano and Micro-tomography* were combined to provide an understanding of geopolymer gel chemistry, nano- and micro-structure in two and three dimensions, and the influences of seeded nucleation and precursor chemistry in these key areas.

The application of advanced characterization methods in recent years has brought the understanding of many aspects of geopolymer chemistry, when the analysis of the aluminosilicate binder gel was considered intractable due to its disordered (“X-ray amorphous”) nature.

Thank to these new techniques is now better understood the influence of compositional parameters on nanostructure and both gel structure and reaction kinetics that can be manipulated through methods including seeding, temperature variation, and careful mix design.

Unfortunately, these techniques are not so easily accessible and cannot be use for investigate a big number of samples produced in the daily laboratory practice.

For this reason, usually traditional techniques (which will discussed in more detail in chapter ...) are used to monitor the macroscopic characteristics such as compactness, porosity, mechanical strength, color, etc ...

Another big problem related to geopolymeric characterization is the kinetics of reaction that is briefly described below.

1.1.2 Geopolymerization mechanism and kinetic

In the 1950s Glukhovsky [13] proposed a general mechanism for the alkali activation of materials primarily comprising silica and reactive alumina. The Gluhhovsky model divides the process into three stages: (a) destruction–coagulation; (b) coagulation–condensation; (c) condensation–crystallization. More recently, different authors have elaborated and extended the Glukhovsky theory and applied the accumulated knowledge about zeolite synthesis in order to try to explain the geopolymerization process [14,15,16,17,18].

Figure 3 and 4 present a highly simplified reaction mechanism for geopolymerization. The theoretical processes occurring in the transformation of a solid aluminosilicate source into a synthetic alkali aluminosilicate here are shown [19].

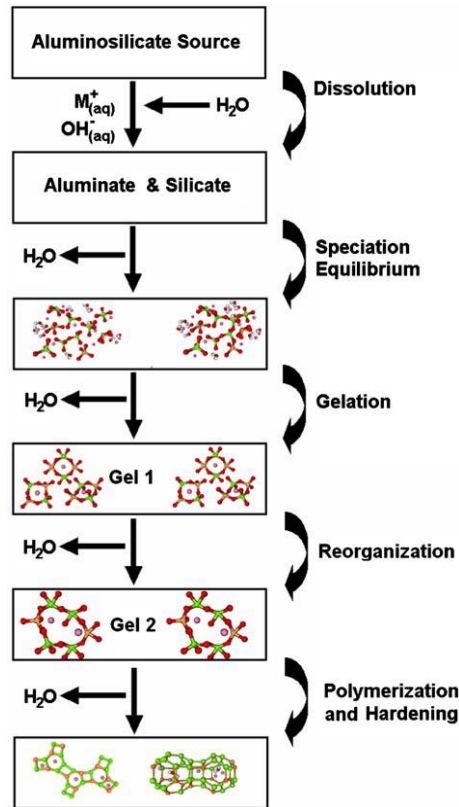


Figure 3 - Conceptual model for geopolymerization [19]

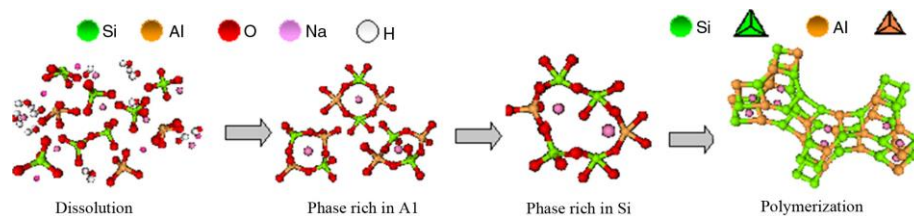


Figure 4 - Model proposed for N-A-S-H gel formation [15].

Though presented linearly (figure 3), these processes are largely coupled and occur concurrently. The dissolution of solid particles at the surface resulting in the liberation of aluminate and silicate species (most likely in monomeric form) into solution has always been assumed to be the mechanism responsible for conversion of the solid particles during geopolymerization.

Once in solution the species released are incorporated into the aqueous phase, which may already contains silicate species present in the activating solution.

A complex mixture of silicate, aluminate and aluminosilicate species is thereby formed, and the speciation equilibria within these solutions have been studied extensively [20,21]. Dissolution of amorphous aluminosilicates is rapid at high pH and this quickly creates a supersaturated aluminosilicate solution. In concentrated solutions this results in the formation of a gel, as the oligomers in the aqueous phase form large networks by condensation. This process releases the water that was nominally consumed during dissolution. The time for the supersaturated aluminosilicate solution to form a continuous gel varies considerably with raw material processing, solution composition and synthesis conditions [22,23,24].

After gelation the system continues to rearrange and reorganize, as the connectivity of the gel network increases, resulting in the three-dimensional aluminosilicate network commonly attributed to geopolymers. These processes of structural reorganization determine the microstructure and pore distribution of the material, which are critical in determining many physical properties [19,25].

Because the dissolution, reorganization and condensation reactions occur concurrently, making it difficult to pinpoint the exact reaction events taking place during the geopolymerization process, thus advanced analytical techniques are very useful to better understanding these chemical mechanisms.

Also in this case *In situ X-ray PDF* analysis, is ideally suited to probing local structural changes occurring on the relatively rapid time scale of the geopolymerization reaction and therefore can provide associated kinetic information due to the high flux of the Synchrotron source and the rapid data collection time [26].

This analysis is used to quantify the extent of reaction as a function of time. It is also possible to assess the influence of some parameters, as concentration of alkali or the presence of free silica on the reaction kinetics and therefore extract information regarding the chemical mechanisms occurring during the reaction.

Nevertheless, for complex amorphous systems such as geopolymer binders are needed complementary atomistic simulations, for example “total energy calculation” techniques to ensure that structural representations not only agree with the experimental data but are also thermodynamically realistic [27].

Obviously these techniques are intended only a specific case, while a lot of studies are still conducted by traditional techniques as FTIR, mechanical tests, etc... [28].

1.1.3 Raw materials

It is shown that the raw materials and processing conditions are critical in determining the setting behavior, workability, chemical and physical properties of geopolymeric products [29].

Among aluminosilicate raw materials, kaolinite, feldspar, industrial solid residues such as fly ash, metallurgical slag, mining wastes etc.. can be used as solid raw materials in the geopolymerization technology.

The reactivity of these aluminosilicate sources depends on their chemical and mineralogical composition, morphology, rheological properties and glassy phase content. The main criteria for developing stable geopolymer are that the source materials should be highly amorphous, to possess sufficient reactivity and to be able to release easily aluminium. In fact it is well known that the availability of aluminum controls to a large degree the properties of geopolymers [30]. The amount of available aluminium, in term of “its release throughout reaction”, affects the geopolymeric strength, acid and thermal resistance and the microstructure [31].

In addition to the reactive aluminosilicate component a chemical activator is required to initiate the geopolymerization reaction.

The composition of alkaline activator used (in solution or in solid state) are formed by these main activators: sodium hydroxide (NaOH), potassium hydroxide (KOH), sodium silicate (Na_2SiO_3) and potassium silicate (K_2SiO_3). These reagents may be used alone or in mixture among them.

Their role is to leach the monomers of Si and Al from the initial raw material thanks to their high pH and finally stabilize the aluminum negative charge due to four-fold coordination. Several studies have shown that the type of cation and the ratio in which they are used, also can affect some mechanical, physical or microstructure aspects of the binders.

NaOH is the most commonly used activator hydroxides in the geopolymer synthesis, being both cheaper and more widely available. It was also the most studied with potassium hydroxide.

As described by some authors the sample strength is strongly dependent on the Si/Al, Si/ M^+ , Al/ M^+ and $\text{H}_2\text{O}/\text{M}^+$ ratios [19-22], for this reason to identify the “correct

stoichiometric ratios” is the basis of the characteristics of the final geopolymeric product.

It is very important that the amount of moles of M^+ and OH^- is sufficient to ensure a good geopolymerization.

As reported by Rowles [4], in samples with low alkaline solution content, there would be both insufficient OH^- to completely dissolve $Si4^+$ and $Al3^+$ and insufficient Na^+ to allow for complete polymerization of the network (residual aluminosilicate powder in the sample may weaken it). On the contrary, in samples with high alkaline activator content, there would be excess OH^- , allowing for a complete dissolution of $Si4^+$ and $Al3^+$, however an excess of alkali would also be left in the sample, weakening the structure.

In fact, the formation of easily soluble components, such as sodium and potassium carbonates or other more reactive species could cause, in particular environmental conditions, the formation of *efflorescence*, very negative for structural and aesthetic aspects.

And the Silicon?

In geopolymer gel the role of the “structural skeleton” is assigned to silicon. Consequently, its quantity and its ability to form bonds directly affect the final performances of the geopolymer binder.

It seems certain that the compression resistance is associated with the Si content: geopolymers with lower silicon content cannot form large geopolymer networks sufficient to have a high structural integrity, while geopolymers with high silicon content are able to construct much larger networks (in chapter 3 will be describe some aspects in the specific case of metakaolin precursor).

Summarizing, the properties of geopolymers can be optimized by proper selection of raw materials, correct proportions of mixture and processing design to suit particular final applications [4].

Their characteristics are mainly based on stoichiometric ratios that determine the liquid–solid ratio of geopolymer binders. The relationship between the compressive strength and SiO_2/M_2O ratio showed that an increase in alkali content increases the compressive strength of geopolymers attributable to the formation of the aluminosilicate three-dimensional network [5,32,33,34,35,36].

Geopolymers are a very complex class of materials characterized by a large number of variables. These are related to the chemical composition of raw materials and the “unlimited” possibilities to vary the molar ratios to work with.

It is difficult to determine the right correspondence between the molar ratios and the final micro-nano structure in order to improve the properties of the end products.

Not less important is the variability of the raw materials in terms of nature, availability, mixtures, etc. It can cause some problems from the point of view of production process, in particular in industrialization perspectives or in technology transfer.

Despite this, today an increasing number of researchers are studying these materials in order to improve their performances and apply them in various fields.

1.1.4 Why geopolymers are so interesting?

The first reason that why geopolymers are gaining increasing recognition and interest after more than 100 years of occasional use, is related to potential reduction of CO₂ emissions when are used in place of Portland-based materials.

In fact most of the raw materials used for geopolymeric production is generally derived (except metakaolin) from industrial by-products (fly ash, blast furnace slag, etc..), that are usually considered as “low environmental impact” [13].

Another reason is that geopolymers can exhibit a wide variety of properties and characteristics such as high compressive strength, low shrinkage, fast or slow setting, acid resistance, fire resistance and low thermal conductivity.

They can also be tailored according to the specific applications in terms of both technical and commercial requirements.

For these advantageous properties, the geopolymer is a promising candidate for the development of various sustainable products as building materials, concrete, fire-resistant coatings, composites reinforced and in addition as a solution for the waste immobilization from chemical and nuclear industries.

Many are the fields of application. The first is certainly the *building field*. It is estimated that the CO₂ emissions from the cement and associated aggregates industries could be reduced by approximately 80% through use of geopolymer technology.

The efficiency and potential of these cements have been amply proven by the exhaustive researches conducted in several countries such as Russia, Ukraine, Poland,

Finland, Japan, China, United States, Canada, India, Australia, Spain, United Kingdom and many others, including Italy [18,37,38,39,40,41,42].

The reached experience has shown that these materials are exceptionally effective under very severe service conditions. Moreover, unlike traditional cements, they have poly-functional properties and can be successfully used where high strength is needed in combination with quick hardening or corrosion or fire resistance [38,32].

More recent contributions have likewise been forthcoming from academic institutions scattered around the world and private companies such as *Zeobond* and *Ceratech*, which have clearly placed their stakes on alkaline activation-based innovation. The joint findings of all these actors have led to the development of a series of technologies that capitalize on the enormous operating versatility of alkaline cements and concretes.

The technologies in place today are briefly described below.

- In concrete technology raw materials are poured into a mixer, dry or in solution, and the components are simply mixed
- In cement technology all the raw materials are ground jointly. The end product is packaged in bags for subsequent use in much the same way as conventional Portland cement.
- With precasting technology, precast elements can be made from alkaline concretes or alkaline cements made as described above. The most significant characteristic of precasting technology may be that it accommodates thermal curing of the material.
- Other technologies are in progress, in particular in non-structure applications, for example, soil stabilization or immobilization of toxic and hazardous waste.

Other industrial uses include: lightened parts, insulator panels [43,44,45,46,47], filters and membranes (for micro- and ultra-filtration, separation, particulate environmental clean-up and reuse, and molten metal filters), radiant burners, gas or chemical sensors, support materials for catalysis or adsorbents [48,49,50] biomaterials [51], pastes for 3D printing and much more.

1.2

Use of geopolymers in Green Building



Green building (also known as green construction or sustainable building) refers to both a structure and the using of processes that are environmentally responsible and resource-efficient throughout a building's life-cycle: from siting to design, construction, operation, maintenance, renovation, and demolition. In other words, green building design involves finding the balance between homebuilding and the sustainable environment.

Currently, World Green Building Council is conducting researches on the effects of green buildings on the health and productivity of their users and is working with World Bank to promote Green Buildings in Emerging Markets through EDGE (Excellence in Design for Greater Efficiencies), Market Transformation Program and Certification.

Although new technologies are constantly being developed to complement current practices in creating greener structures, the common objective of green buildings is to reduce the overall impact of the built environment on human health and on the natural environment.

Currently the building sector's environmental impact is enormous, as it accounts for the use of 40% of the natural resources extracted in the industrialized countries, the consumption of 70% of the electricity and the 12% of potable water, and the production of 45-65% of the waste disposed to landfills [52]. Moreover, it is expected to increase, due to the growth in global population from 6.5 billion in 2005 to approximately 9.0 billion in 2035 [53]. In this scenario, the mitigation of the environmental impact of buildings is a primary issue [54].

In the past decades, a great effort was addressed toward the reduction of the energy required in the operation phase of the building and the adoption of more efficient technical solutions and materials [55] led to an improvement in the energetic performance of buildings during their service life.

The contemporary impulse to the exploitation of renewable energy sources led to a rapid growth of the Zero Energy Building (ZEB) concept [56] implying a zero annual balance between the energy used for the building's operation and the energy gained from renewable sources, such as in 'solar houses' [57].

The Directive 2010/31/EU of the European Parliament and of the Council of 19 May 2010 on the energy performance of buildings establishes the target of 'near zero energy buildings' for public buildings at 2018 and for all new buildings at 2020 [56].

Meanwhile, growing attention was addressed also to the pre-use phase of the building [6], i.e. to the environmental impact of building materials (raw materials extraction, manufacturing process and delivering to the construction site).

Such impact can be quantified by means of the parameters identified in the Life-Cycle Assessment (LCA) procedure (ISO 14040), in terms of energy requirement, contribution to greenhouse gases production, water depletion, etc.

The LCA can assess a full range of impacts associated with all "cradle-to-grave" stages of a process: from extraction of raw materials through materials processing, manufacture, distribution, use, repair and maintenance and disposal or recycling.

1.2.1 What are "green building" materials?

A univocal and universally accepted definition of 'green building materials' still doesn't exist and they are generally considered as environmentally friendly [10] or environmentally responsible materials. According to a more sensible common perception, green building materials can be defined as:

- sustainable during their whole life-cycle, where their sustainability can be quantified by the LCA methodology,
- not hazardous for human health, i.e. not leading to negative effects in terms of indoor air quality. In particular, they must not cause indoor pollution, hazardous fibres dispersion, radon emission, biological pollutants proliferation and uncomfortable indoor climatic conditions, both of the aspects to be jointly considered.

In dealing with such definition, a key issue immediately arises, that is the inexistence of a 'perfect green building material' because the manufacturing, transportation, placing and disposing/recycle of materials always imply a not zero impact. For this reason, in every design process the most green materials should be chosen among the market

available ones, on the basis of the best available technologies and the required materials performance [54].

The “greenness” requirement, materials must fulfil a wide range of requirements established by national laws, national/international standards, codes of practice and local building habits, at least in terms of:

- mechanical properties (for structural materials), such as strength, stiffness, behavior in case of seismic actions, etc.
- thermal performance, in order to achieve a satisfactory energetic behavior during the operating phase
- acoustic performance, in order to achieve a satisfactory indoor comfort
- durability in the specific environmental context where the building will be located
- weight and dimension limits, in compliance with the specific features of the building
- safety during the materials handling and placing, as well as in case of fire
- specific performances connected to the use of buildings
- aesthetic outcome, also in connection with the local construction traditions
- cost

Geopolymeric materials and in general all “alkali activated materials” can be considered “green building materials” because can be formed from industrial waste (such as fly ash, rice hull ash, etc..) substituting completely or partially conventional OPC [58].

As mentioned above, Australia is certainly the Country that has best developed and applied the “geopolymer technology”.

Private companies and Universities are particularly active in the study of these materials and their research has produced tangible results.

For example, thanks to the University of Queensland's Global Change Institute (GCI), in conjunction with Wagners Company, in 2013 it was built the world's first building to successfully use geopolymer concrete (called Earth Friendly Concrete (EFC)) for structural purposes.

The 33 precast floor beams in the new building were made from a binder that contains ground granulated blast furnace slag, a waste product from steel production, and fly ash, a waste product from coal fired power generation but no normal Portland cement [59,60].

Another example could be E-Crete™ a geopolymer concrete produced by Zeobond and used since 2006 in a broad range of applications, for example driveways, footpaths, house-slabs, in-situ pours, pre-cast concrete wall panels, concrete pavers and more.

E-Crete™ is made at ambient temperatures, in the same ways as ordinary cement-based concrete and using the same equipment. This means that anyone can use geopolymers by using similar techniques and staff as for cement-based concrete. In addition, the setting time of geopolymers can be manipulated much in the same way as cement-based concrete [61].

1.3

Use of geopolymers in Cultural Heritage and artworks



In the field of Cultural Heritage and artworks, geopolymers may be used for many specific applications, especially as regards inorganic materials, typically present in the architectural structures and archaeological sites .

Among the materials with which they can interact there are Roman cements, lime-based mortars, natural stones, bricks, ceramics, glasses, etc ...

The history of geopolymer *concrete* seems to be deeply connected to the art; the same Davidovits suggested that some great works created in the past, such as the Pyramids of Egypt, are formed by artificial agglomerate blocks based on geopolymeric binder. This hypothesis, which would seem justified by the availability of raw materials in the surrounding area of the Pyramids, such as limestone and natron, is not entirely shared by the scientific community and currently the archaeometric studies are in progress.

1.3.1 Geopolymers and modern artworks

An example is the “GEOPOLYSTONE technology” (CORDI-Géopolymère) that is the modern equivalent to the 5000 year old Egyptian technique. This technology is based on the use of modern geopolymeric binders and cements and in the field of art allows to reproduce artworks and surface finishes with very subtle details.

In general, the Geopolystone® can be applied directly on various surfaces, ideal for facades, pediment and outlines of cornices. The advantage of this material/process is that no additional protection with any external coating is needed because presents high UV and IR resistance, excellent freeze-thaw behavior, excellent wet-dry behavior and long term stability [62].



Fig 5 - Collection of various statues in geopolystone (reconstituted natural stone) [62]

Obviously when it comes to contemporary applications, there is no the need to observe particular standards of quality, except that the material satisfies the artist's requirements. On the contrary regarding the restoration field much more limitations are present. In addition to criteria observed in green building more severe rules are necessary to take in consideration, in particular physical and chemical compatibility but also mechanical properties such as hardness, strength, adhesion capacity and more. A very important aspect is the *“reversibility concept”* [63].

1.3.2 Geopolymers and ancient artworks

The conservation-restoration of cultural heritage focuses on protection and care of tangible cultural heritage, including artworks, architecture, archaeology and museum collections. Conservation of cultural heritage involves collection care and management through tracking, examination, documentation, exhibition, storage, preventative conservation and restoration.

“Restoration is generally understood as any kind of intervention that permits a product of human activity to recover its functions... us consider the variety of products of human activity to which the particular intervention we call restoration should be applied” [64].

The theory that we know today and which now is shared in many Countries of the World is born thanks the "Italian school."

The biggest contribution was given by Cesare Brandi; he was certainly the most important figure for the theorization and diffusion, in Italy and also within the wider international context, of a modern restoration culture [65].

Brandi defined the restoration as: *“Restoration is the methodological moment in which the work of art is appreciated in its material form and in its historical and aesthetic duality, with a view to transmitting it to the future”*

In fact: *“The work of art is universal regardless of time and fashion in which it was created ”* [66]. *“The material form of the work of art must necessarily take precedence because it represents the very realm of the image’s manifestation; it ensures the transmission of the image to the future, and thus guarantees its perception within human consciousness [...],*

Matter represents contemporaneously both the “time” and the “place” of a restoration” [64].

From this, the first Brandi's principle is: "Only the material form of the work of art is restored" while the second, that underlines the importance of the historical and aesthetical aspects of work of art is: "Restoration must aim to reestablish the potential unity of the work of art, as long as this is possible without producing an artistic or historical forgery and without erasing every trace of the passage of time left on the work of art".

On the basis of the theories exposed, in all restoration approach/projects should be taken into consideration various "criteria" that satisfy both the "preventive conservation" that the "restoration intervention".

Preventive conservation involves any actions taken to prevent or delay the deterioration of cultural heritage and is a practice of preservation that provide a stable environment to minimize further damage or deterioration. Generally the damage occurs from two main sources, the Environment and Human "activity".

Restoration intervention is the practice of mitigating further deterioration. The goal is to "treat" an artefact, in order to ensure its safety during its storage or its new exposure. In some case, for example in archeological sites, conservation/restoration approach is a "**minimal intervention**" that is generally limited to "*la salvaguardia dello status quo*".

For any other restoration interventions these principles should be followed:

- **visibility of the intervention:** *"L'integrazione dovrà sempre essere riconoscibile [...]. Quindi dovrà essere invisibile alla distanza a cui l'opera d'arte deve essere guardata ma immediatamente riconoscibile e senza bisogno di speciali strumenti, non appena si venga ad una visione ravvicinata"* [67]
- **reversibility of the intervention:** *"Il terzo principio si riferisce al futuro: e cioè prescrive che ogni intervento di restauro non renda impossibili, anzi faciliti gli eventuali interventi futuri"* [67].

For this all innovative materials such as geopolymers, are viewed with particular skepticism and their application is certainly not easy or obvious.

Many tests are necessary in order to assess:

- the chemical stability in terms of release of soluble fractions and potentially harmful for the original artifact,

- the physical stability in terms of low thermal expansion, shrinkage, water penetration capacity (porosity) and color
- the mechanical stability
- the reversibility, concept that must be applied to any material and / or product (consolidant, protective, mortars, etc ...).

In the past, some research groups have tried to use the geopolymers in various applications [68,69,70,71,72,73] but perhaps the most significant one concerns the restoration of a terracotta statue. In this application the geopolymer has been used with three different functions: as an adhesive, as a filler of gaps and as a reinforcing material [74].

Today, at least in Italy the research groups working on geopolymers in the field of cultural heritage are very few. One certainly very active is that of the CNR-ISTEC of Faenza, an Institute of National Council of Research in which I carried out my research activity for this PhD thesis [75,76,77].

Currently, some interesting works have been presented concerning the application of geopolymers in the field of restoration, once again confirming that these, with the right devices and on the basis of detailed studies, represent a very promising material in the cultural heritage field [78,79,80,81,82,83,84,85,86].

1.4

Research Aims

The aim of this thesis is to deepen the studies related to the class of geopolymers based on metakaolin in order to find new formulations that could satisfy specific properties.

Because geopolymers are considered very interesting for their versatility, the first purpose of the research is to verify that attribute through the design and formulation of a wide range of mixtures capable of developing specific final characteristics also through the introduction of inorganic and organic components.

The evaluation of important properties in order to utilize an innovative material, such as density, workability, setting time, mechanical strength, porosity and chemical stability is the basis of this experimentation.

Assessing the influence of each introduced component on the finished product it is possible to direct it, towards the research fields of this thesis.

Chapter 2

Sample's preparation and analytical techniques

2.1

Kaolins Preparation methods

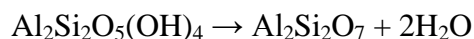
What is Kaolin?

Kaolin is fine clay mainly constituted by kaolinite with lesser amounts of illite, gibbsite, quartz and anatase. It derives by chemical weathering of aluminum silicate rocks.

The chemical structure of kaolinite is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (theoretically 39.8% alumina + 46.3% silica + 13.9% H_2O), arranged in two crystalline layers of silicon-oxygen tetrahedral layer joined to alumina octahedral layer.

Kaolin has been the basic raw material used in the ceramic industry, especially in the production fine porcelains. Large quantities are used also in paper coating, filler, paint, plastics, fiberglass, catalysts, and other specialty applications.

Metakaolin (MK) is one of the main raw materials for the production of geopolymers, because it is characterized by high reactivity. It can be considered an artificial material because derives from chemical transformation of kaolin (by endothermic dehydration):



The high contents of silicon and aluminum oxides of MK confer to geopolymer excellent characteristics of stability and refractoriness, ideal for the building field. Unfortunately, the high cost of the kaolin and the expensive production process create some disadvantages..

For this reason, the MK is not strictly considered an “environmentally friendly” and in the production of geopolymers is mostly used as a model (thanks to its constant chemical and mineralogical compositions) to better understand the kinetic mechanisms and the chemical-physical behavior of the final products.

This aluminosilicate source presents high reactivity mainly for two aspects: the first depends on the amount of Al present and "available" to the reaction, the second

concerns the microstructure of the powder, which being laminated presents a very high surface area.

The kaolin amorphization process is very important because it determines the capability of being more or less reactive with alkaline solutions.

Generally the most widely used process is the thermal activation, carried out at temperatures of 650-750 °C.

This calcination induces:

- change of the Al coordination, from the octahedral Al (Al(VI)) originally present in kaolin, to Al(V) and Al(IV). This data is widely used today to estimate the reactivity of MK by NMR spectroscopy toward the alkaline attack,
- gradual process of dehydroxylation and disordering structural deformation of the layered clay structure, which is also responsible for the reactivity of the MK in alkaline conditions.

Another reason that makes the MK an excellent raw material is that the formation of “geopolymer units” is particularly fast and efficient because -Si-O-Al=O and $\text{-Si-O-Al-O-Al-O-Si-}$ bonds are originally present deriving from the dehydration of the -Si-O-Al(OH)_2 units present in the kaolinite. In particular the -Si-O-Al=O bonds come from the loss of a water molecule from the same -Si-O-Al(OH)_2 unit, while $\text{-Si-O-Al-O-Al-O-Si-}$ bonds arise from the loss of water from two -Si-O-Al(OH)_2 contiguous units.

During this PhD research, two types of MK were used to produce geopolymeric binders. Both derived from commercial kaolin powders named BS4 and BS6 and were “treated” in the CNR laboratories.

The BS4 was made reactive through two different processes: the traditional thermal activation and an innovative method that is the mechano-chemical activation.

This activity was carried out within MECAGEOPOLY project "Mechano-chemistry: an innovative process in the industrial production of poly-sialate and poly-silano-sialate binders used in building construction" (2013-2015). This project was financed by CNR within the frame of the Project “Factory of the Future”, funded by Italian Ministry of Research and Education (MIUR). In this "Flag Project" one of the objectives was to find an innovative "activation" method for aluminosilicate natural raw materials (kaolin and tuffs), obviously more green and economical than conventional ones.

The MECAGEOPOLY Project was aimed at proving that:

- a) the mechano-chemical activation of kaolins is a valid alternative to the thermal treatment at 650-750°C for the industrial production of Poly-Sialate-Siloxo (PSS) geopolymeric binders to be used in building construction (field) and in other industrial applications;
- b) the geopolymeric binders obtained by mechano-chemical activation of kaolins have similar properties than those obtained by thermal treatments;
- c) the mechano-chemical treatment can be exploited for making geopolymeric binders from other alumino-silicate rocks, such as quarry wastes of volcanic tuff cemented by glass (welded tuffs) or by authigenic minerals (zeolites), that are difficult or impossible to activate by thermal processes;
- d) the mechano-chemical process is easier to control than the thermal process and it is feasible at an industrial scale.

The BS6, the second MK used in this research, was treated only with the thermal process.

This MK, similar to BS4 in terms of chemical and mineralogical composition, was chosen in order to assess if changing the starting raw material, but maintaining unaltered the various working parameters (molar ratios, mixing times, curing temperature, etc ..) it is possible to obtain similar final products in terms of chemical-physical characteristics and mechanical performances.

This problem is very important from the point of view of industrialization, in particular for an innovative material.

Thanks to the obtained results a new project focused on geopolymeric binders was proposed and financed by Emilia Romagna regional funding “Tecnopolo-Mitai-Sviluppo e messa a punto di materiali e tecnologie innovative ed ecocompatibili per il restauro e la conservazione dei Beni Culturali – Sviluppo di materiali compositi geopolimerici alleggeriti e colorati”.

Despite the type of MK, for the production of geopolymeric binders the working procedure has been the following:

- characterization of raw materials and selection of the activation solution (silica glass and alkali hydroxide),

- development of suitable "formulations" (assuming a degree of aluminum reactivity from 75 to 90%) to obtain potassium-based poly-siloxo-sialate geopolymers (K-PSS) composed of the following monomeric units:
 $\text{K}^+ [-(\text{SiO}_2-\text{AlO}_2-\text{SiO}_2)-]_n \cdot n\text{H}_2\text{O}$ with $\text{Si}/\text{Al} = 1.8-2$. This specific type of geopolymer was selected because it produces nanocrystal gels with a sufficient mechanical strength to be used in building industry [2],
- physical, mechanical and microstructural characterization of the K-PSS binders obtained both mechano-chemical and thermal treatments and comparison of their properties, in order to evaluate their repeatability and reproducibility,
- synthesis and characterization of geopolymers composites adding different types of aggregates as sand, perlite, basalt fiber, etc... (Chapter 4).

2.1.1 Calcination process

The calcination process consists in subjecting the material to an “adequate” thermal cycle, in order to obtain an evident change in the crystalline phase composition.

Temperature, time of the process and different "kiln technology" can induce different features to the final product.

Already at 550 °C, the calcination treatment causes in MK the loss of the lattice water from kaolinite and its transformation into metakaolinite, with a disordered (amorphous) structure. This process is known as “de-hydroxylation” and plays a central role for obtaining a reactive material.

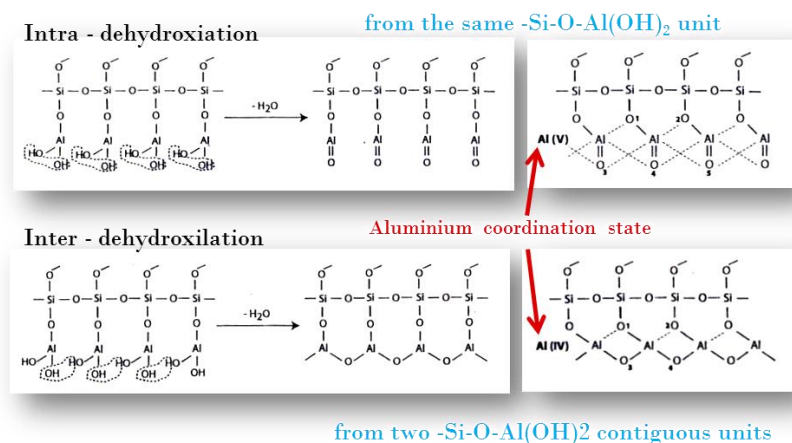


Figure 1- Schematic dehydroxylation of metakaolin [2]

The dehydroxylation (fig 1) seems favor different coordination states of Aluminum:

- penta-coordinated (Al(V)) in the $-\text{Si-O-Al=O}$ units
- tetra-coordinated (Al (IV)) in the $-\text{Si-O-Al-O-Al-O-Si-}$ units.

The relative contents of Al(V) and Al(IV) with respect to the octahedral Al (Al(VI)), originally present in kaolin are widely used today to estimate the reactivity of MK; Al(V) seems to be the most reactive one.

So, it is important to know all the variables that influence the dehydroxylation process, such as kaolin characteristics and heating parameters.

Calcination at too high temperature, in fact, results in the appearance of both crystalline and non-crystalline phases, for example γ -alumina or mullite, which can provoke a decrease of reactivity.

2.1.2 Mechano-chemical process

This process consists into grinding the material in a mill composed of a metal jar containing the moving bodies (one or more concentric rings and a cylinder).

The rotating motion is transmitted to the mill by the shaft of an electric engine, whose speed can be controlled.

When the engine is activated, the rings and the cylinder, that are free to move inside the jar, are subjected to centrifugal forces pushing them against the internal walls of the jar. Pressures proportional to the mass of the moving bodies (M) and the rotational speed of the engine (in r.p.m.) are thus generated between the moving bodies and the internal walls of the jar.

The material to grind is not only subjected to pressure but also to impact and friction action of the moving bodies.

The amount of energy adsorbed from the material (for the chemical conversion) depends on several parameters, including the friction coefficient of the material, the ratio M/m used in the mill, the rotational speed of the electric motor and the grinding time [87,88,89]. In this case, the result is chemically activated (MK-M) kaolin, with characteristics as reactivity, color, grain size and specific surface area of the particles very different to MK BS4 treated by thermal process (MK-T) [90].

All these aspects have been analyzed using several analytical techniques, in particular the degree of amorphization, basic for the geopolymers production, caused by the

grinding times. The mechano-chemical treatment involves all the mineral phases present in the raw kaolin, increasing the reactivity of the treated powders.

2.1.3 Importance of the formulation

As it known, the geopolymers can be opportunely prepared and tailored by selecting the reactive raw materials and by formulating the right proportions among the different components, i.e. reactive powders, additives and alkaline solutions. As reported in Chapter 1, the characteristics of geopolymers (fig 2) are mainly based on some important ratios: Si/Al; alkalis/ Al_2O_3 and $\text{H}_2\text{O}/\text{alkalis}$. These ratios permit to tailor the physical and mechanical properties of the geopolymers.

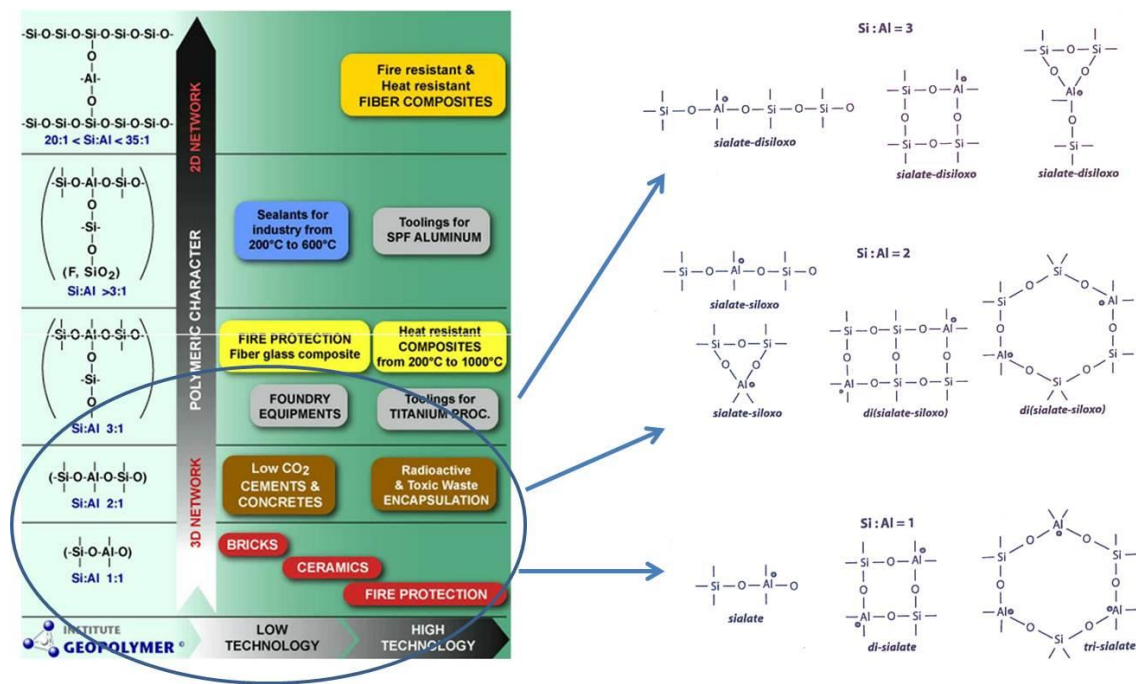


Fig 2. Hypothetical geopolymeric structures based on Si:Al ratio [2]

The following molar ratios were chosen to Mecageopoly activity:

$\text{Si}/\text{Al} = 1.8$; it means $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.6$; $\text{K}_2\text{O}/\text{Al}_2\text{O}_3 = 1$.

The $\text{H}_2\text{O}/\text{K}_2\text{O}$ ratio varies depending on the amount of alkaline solution introduced.

In the calculation of the ratios, particular attention was devoted to the percentage of aluminum. We started from the consideration that not all the aluminum content in the raw kaolin is reactive; it means that not all the Al is involved in the reaction with the

alkaline solution. So, also supported by the NMR results, we have prepared several mixtures considering different percentages of Al reactive, more precisely 90, 85, 80 and 75%. In this way, the ratios Si/Al and K_2O/Al_2O_3 are always constant, but the contribution of Al in the reaction of geopolymerization varies.

In the case of MK-M, not only the aluminum determines the reactivity of the powder but all mineralogical phases involved in the activation process, such as quartz.

For this reason, it was necessary to monitor by NMR the coordination change of Al and Si as a function of the grinding times.

Initially, the MK powders were considered comparable on the basis of the chemical characteristics obtained from analytical testing (XRF, NMR, FTIR XRD), then other properties as workability, physical and mechanical properties of the various products have been considered in order to achieve the better working conditions.

2.1.4 Pozzolanic activity

The pozzolanic activity is defined as the capacity of the material to react with calcium hydroxide in presence of water. For the evaluation of the reactivity of MK in terms of “ability to fix calcium hydroxide in the presence of water to produce reaction products with new binding capacity” we made use of a variant of the method called "modified Chapelle test" [91].

This method is based on the ability of alumino-silicate powder (in our case MK), to react with calcium hydroxide (portlandite) in the presence of water to form, at room temperature, new alumino-silicate species based of calcium stable over time (typical phases of the chemistry of cements).

The formation of such species may give indirect information on the ability of the material to bind with various cations carried by an aqueous medium.

The final reactivity is obtained by calculating, thanks thermogravimetric analysis, residues of hydroxide and calcium carbonate, which are prepared taking into account their molecular weights and their relationship with the water, until obtaining a final value expressed in percentage. This value corresponds to the amount of portlandite reacted during the process and therefore, indirectly of the MK ability to react in that particular "chemical system".

2.2

Analytical methodologies and experimental conditions

Analytical techniques reported in this chapter have been used to provide information about raw materials and geopolymers produced during this PhD.

As discussed in the Chapter 1, geopolymers are very complex materials due to their amorphous nanostructure. Therefore in order to investigate their intrinsic characteristics and synthesis mechanisms, advanced analytical techniques such as “synchrotron light” should be required. This light allows to see the details of the structure and behavior of atoms and molecules, helping to solve the most disparate problems in various fields.

Unfortunately, this technique is not so easily accessible and cannot be use to investigate all samples produced in the daily laboratory practice.

For this reason, in general and in this specific study, traditional techniques are used to monitor microscopic and macroscopic characteristics such as compactness, porosity, mechanical strength, color, etc ...

2.2.1

Chemical properties

2.2.1.1 X-Ray Fluorescence (XRF)

X-ray fluorescence (XRF) is an X-ray technique used for ordinary and relatively non-destructive chemical analyses of rocks, minerals, sediments and fluids. It is typically used for bulk analyses of larger fractions of geological materials. The relative low cost of sample preparation, the stability and the ease of use of X-ray spectrometers make this one of the most widely used methods for analysis of major and trace elements in rocks, minerals, and sediments.

The XRF method depends on fundamental principles that are common to several other instrumental methods involving interactions between electron beams and X-rays with samples.

The analysis of major and trace elements in geological materials by x-ray fluorescence is made possible by the behavior of atoms when they interact with radiation. When materials are excited with high-energy, short wavelength radiation (e.g., X-rays), they can become ionized. If the energy of the radiation is sufficient to dislodge a tightly-held inner electron, the atom becomes unstable and an outer electron replaces the missing

inner electron. When this happens, energy is released due to the decreased binding energy of the inner electron orbital compared with an outer one. The emitted radiation is of lower energy than the primary incident X-rays and is termed fluorescent radiation. Because the energy of the emitted photon is characteristic of a transition between specific electron orbitals in a particular element, the resulting fluorescent X-rays can be used to detect the abundances of elements that are present in the sample.

Analytical conditions

1 gram of powder of sample was mixed with 9 grams of a fondant mixture made by lithium meta- and tetra-borate and lithium bromide.

A fluxer machine [CLAISSE Fluxy mod.] was used to form a glassy disk to be used for the analyses..

The analysis was performed with a X-Ray fluorescence spectrometer [PANalytical mod. AXIOS ADVANCED], at the Department of Industrial Chemistry Laboratories "Toso Montanari", University of Bologna. An uploaded set of standards "Omnia" was used for the quantitative analysis. The results are expressed in percentage by weight of the oxides and normalized to 100.

2.2.1.2 NMR spectroscopy

NMR spectroscopy is one of the principal techniques used to obtain physical, chemical, electronic and structural information about the resonant frequencies of the nuclei present in the sample (molecules) thanks to either the chemical shift, Zeeman effect, or the Knight shift effect, or a combination of both.

Most applications of NMR involve full NMR spectra, that is, the intensity of the NMR signal as a function of frequency.

NMR is a powerful technique that can provide detailed information on the typology, dynamics and three-dimensional structure of molecules in solution and the solid state exploiting the magnetic properties of certain atomic nuclei.

The intramolecular magnetic field around an atom into a molecule changes the resonance frequency, thus giving access to details of the electronic structure of a molecule and its individual functional groups.

Many scientific techniques exploit NMR phenomena to study molecular physics, crystals, and non-crystalline materials.

The principle of NMR involves two sequential steps:

- the alignment (polarization) of the magnetic nuclear spins in an applied, constant magnetic field B_0 ;
- the perturbation of this alignment of the nuclear spins by employing an electromagnetic, usually radio frequency (RF), pulse. The required perturbing frequency is dependent upon the static magnetic field (H_0) and the nuclei of observation.

The two fields are usually chosen to be perpendicular to each other as this maximizes the NMR signal strength. The resulting response by the total magnetization (M) of the nuclear spins is the phenomenon that is exploited in NMR spectroscopy and magnetic resonance imaging. A disadvantage is that a relatively large amount, 2–50 mg, of a purified substance is required, although it may be recovered through a workup. Preferably, the sample should be dissolved in a solvent.

NMR techniques are very useful for:

- characterizing molecular structures;
- monitoring the composition of mixtures;
- studying molecular dynamics and interactions;
- quantifying known and unknown components.

Solid-state nuclear magnetic resonance (MAS-NMR)

In nuclear magnetic resonance, magic-angle spinning (MAS) is a technique often used to perform experiments in solid-state NMR spectroscopy.

By spinning the sample (usually at a frequency of 1 to 111 kHz) at the magic angle θ_m (ca. 54.74° , where $\cos^2\theta_m=1/3$) with respect to the direction of the magnetic field, the normally broad lines become narrower, increasing the resolution for better identification and analysis of the spectrum.

This technique complements X-ray crystallography in that it is frequently applicable to molecules in a liquid or liquid crystal phase, whereas crystallography is performed on molecules in a solid phase. Though nuclear magnetic resonance is used to study solids, extensive atomic-level molecular structural detail is especially challenging to obtain in the solid state.

NMR spectrometers are relatively expensive having a very strong, large and expensive liquid helium-cooled superconducting magnet, because resolution directly depends on magnetic field strength. Less expensive machines using permanent magnets and lower

resolution are also available, which still give sufficient performance for certain application such as reaction monitoring and quick checking of samples.

MAS-NMR Analysis condition

Samples were grinded into fine powder, and aliquots of ca. 110 mg were inserted in 4 mm zirconia rotors sealed with Kel-F caps. Spectra were recorded on a Bruker ASX200 NMR spectrometer. The spinning rate was 12 kHz.

The relative contents of Al(IV), Al(V) and Al(VI) were determined by ^{27}Al NMR by measuring the resonances in a 3 quantum dimension of a 2D map (f1).

NMR Relaxometry

Time-domain NMR is an alternative to classical NMR that offers a number of advantages over solid-state NMR.

In nuclear magnetic resonance (NMR) the term relaxation describes the evolution of the nuclear magnetization that returns to the equilibrium after a stimulation (radiofrequency pulse). The evolution of the nuclear magnetic signal is analyzed in terms of two different processes that are characterized by their own time constants. One process is associated with T1 and it is responsible for the relaxation of the components of the nuclear spin magnetization vector M parallel (longitudinal) to the external magnetic field B_0 . T1 relaxation process describes the redistribution of nuclear magnetic spin populations to reach the thermal equilibrium distribution ("spin-lattice" relaxation). The other process is associated with T2 and it is responsible for the relaxation of the components M perpendicular (transverse) to B_0 . The T2 relaxation process describes the decoherence of the transverse nuclear spin magnetization due to random fluctuations of the local magnetic field caused by other nuclear surrounding spins ("spin-spin" relaxation).

The discipline that study the NMR relaxation process in the time- domain is the Relaxometry. In this case, an exhaustive characterization of the time constants T1 and T2 is needed.

Another approach for the study of the NMR relaxation is in the frequencies domain, and the discipline is called NMR spectroscopy. The analysis of frequency spectrum, that composes NMR relaxation signal, gives information about the structure of a molecule. Indeed, analyzing the so-called "chemical shifts" (frequency shift from a standard

nucleus frequency) it is possible to characterize the surrounding environment of a certain nucleus (functional groups etc.).

The physical phenomenon of ^1H Nuclear Magnetic relaxation, in molecular fluids, is mostly caused by interactions between nuclear spin of nuclei that constitute the fluid. In various hydrogenous liquids, the main source of relaxation is the dipolar relaxation of protons of the same molecule. Usually small molecules (in this case water molecules) are characterized by a fast-rotational diffusion that makes the correlation time short, and thus the relaxation. NMR relaxation is a fundamental phenomenon for investigating the action with surrounding environment. One of the most significant contributions to the relaxation process is related to the diffusion at the surface of confinement structures (walls, pores etc.) where spins experience relaxation at the boundary of liquid-solid.

Polymerization kinetics of the compound BS6 + KSil was monitored by a Time-Domain Nuclear Magnetic Resonance study of the longitudinal relaxation times T_1 s and transverse relaxation times T_2 s of ^1H nuclei.

Analysis conditions

The solid MK powder and geopolymer binder (about 5 g) were put into a "NMR glass tube" (diameter 8 mm) and measurements were executed on 0.47 T electromagnet (JEOL C60) corresponding to a Larmor frequency to the MHz ^1H 20:15. The experiment was run using the portable digital console PC-NMR (s.r.l. Stelar, Mede).

For characterizing the transverse relaxation (T_2) it was used radiofrequency CPMG pulse sequence with the following parameters:

Pulse Length: 3.8 μs , Echo Time = 50 μs , n° Echoes = 1024, Repetition Time = 2 s, n° Scan = 16. Were acquired 31 CPMG (13, 19, 24, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 90, 100, 110, 125, 140, 160, 170, 200, 230, 365, 450, 570, 930, 1050, 1350, 1830, 2310) min.

The constant T_1 , which describes the longitudinal relaxation, was measured using the IR / S sequence (Inversion Recovery - Staggered) setting the following parameters:

Pulse Length: 3.8 μs , n° inversion times = 128 (logarithmically spaced from 50 μs to 400 ms), dwell = 1 μs , n° points = 512, Repetition Time = 2.5 s, n° Scan = 8.

Two IR / S were acquired at 15 min from the sample preparation and the other after 5 h. A "2D relaxometry" measurement (IR-CPMG) was carried out for the characterization of the "relaxation-relaxation T_1 - T_2 " correlation function.

Distributions of T1 and T2 relaxation times have been obtained by calculating the inverse Laplace transform by the UPEN software.

The process was monitored for 15 days from the preparation. The analysis of relaxation times distributions during the polymerization process gives us the capability to distinguish different condition of restriction/trapping of 1H.

2.2.1.3 FTIR

Infrared spectroscopy (IR spectroscopy or Vibrational Spectroscopy) involves the interaction of infrared radiation with matter. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, IR can be used to identify and study chemicals. For a given sample which may be solid, liquid, or gaseous, the method or technique of infrared spectroscopy uses an instrument called an infrared spectrometer (or spectrophotometer) to produce an infrared spectrum. A basic IR spectrum is essentially a graph of infrared light absorbance (or transmittance) on the vertical axis vs. frequency or wavelength on the horizontal axis. Typical units of frequency used in IR spectra are reciprocal centimeters (sometimes called wave numbers), with the symbol cm^{-1} . A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher-energy near-IR, approximately $14000\text{--}4000\text{ cm}^{-1}$ ($0.8\text{--}2.5\text{ }\mu\text{m}$ wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately $4000\text{--}400\text{ cm}^{-1}$ ($2.5\text{--}25\text{ }\mu\text{m}$) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately $400\text{--}10\text{ cm}^{-1}$ ($25\text{--}1000\text{ }\mu\text{m}$), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these sub-regions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

Infrared spectroscopy exploits the fact that molecules absorb frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the vibrational frequency. The energies are affected by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling.

In order for a vibrational mode in a sample is "IR active", it must be associated with changes in the dipole moment.

The Fourier transform infrared spectroscopy requires a Fourier transform to convert the raw data into the actual spectrum.

The total scope of FTIR is extensive. Some of the more common applications are: quality verification of incoming/outgoing materials, de-formulation of polymers, rubbers, and other materials through thermogravimetric infra-red (TGA-IR) or gas chromatography infra-red (GC-IR) analysis, microanalysis of small sections of materials to identify contaminants, analysis of thin films and coatings, monitoring of automotive or smokestack emissions.

Analysis conditions

FTIR analysis of the materials was conducted with an AVATAR 320 Spectrometer. The KBr pellet (Sigma Aldrich, Germany) method was used to prepare the samples, which were scanned at a range of from 4000 to 400 cm⁻¹. For each sample 1-3 mg of powder (MK and geopolymers) was mixed with 150-200 mg of KBr. Spectra were collected and elaborated by OMNIC software.

2.2.1.4 Thermal Analysis

Thermal Analysis (TA) is a group of techniques that study how the properties of materials change with temperature. In practice, thermal analysis gives properties like enthalpy, thermal capacity, mass changes and the coefficient of heat expansion.

TGA

Thermogravimetric analysis (TGA) measures the changes in physical and chemical properties of materials as a function of increasing temperature (with constant heating rate) or as a function of time (with constant temperature and/or constant mass loss). TGA can provide information about physical phenomena, such as second-order phase transitions, including vaporization, sublimation, absorption, adsorption and desorption. Likewise, TGA can provide information about chemical phenomena including chemisorptions, desolvation (especially dehydration), decomposition, and solid-gas reactions (e.g., oxidation or reduction).

TGA is commonly used to determine selected characteristics of materials that exhibit either mass loss or gain due to decomposition, oxidation or loss of volatiles (such as moisture). Common applications of TGA are: materials characterization through

analysis of characteristic decomposition patterns, studies of degradation mechanisms and reaction kinetics, determination of organic and inorganic (e.g. ash) contents in a sample. It is an useful technique for the study of polymeric materials, including thermoplastics, thermosets, elastomers, composites, plastic films, fibers, coatings and paints.

DTA / DSC

Differential Thermal Analysis (DTA) records any temperature difference between sample and an inert reference material underwent to identical thermal cycles

The differential temperature is plotted against time or against temperature (DTA curve or thermogram). Combining TGA-DTA a comprehensive study of materials thermal behavior is possible.

The DSC technique measures the difference of heat flow rate into a sample and a reference material. The two techniques differ since DTA measures a difference in temperature whereas DSC a change in enthalpy. Precisely, DTA measures the temperature variations (endothermic or exothermic) occurring during heating caused by phase changes.

Pozzolanic activity- experimental

A quantity of metakaolin (thermally and mechano-chemically activated) was mixed with an opportune quantity of Ca(OH)_2 (purity 95%, Sigma Aldrich), in 1:1 ratio, and with distilled water (0.5 gram + 0.5 gram + 10 ml). The mixture (3 samples for each one) were poured into a tube and sealed with Parafilm. To favor the complete homogenization and to avoid the separation among the components, the tubes were maintained in agitation for 2 h, in an oscillating shaker at room temperature with a medium velocity.

Then, the tubes were left for 7, 14, 28 days in order to verify the time necessary to develop the complete the reaction. After each period, the samples were prepared for the analysis by recovering and drying at 60°C for 24h the solid fraction. The dried powder were then milled and 10-15 grams were analyzed with thermal instrumentation.

This procedure of determination of pozzolanic reactivity is in accordance to the so-called direct method, which is based on the determination of the amount of un-reacted lime by using thermal analyses. The Chapel test provides the determination of residue of lime by means of chemical procedure.

By using thermal analyses, we can directly observe and calculate the percentage of weight loss in the range of temperature comprised by 450-470°C, in which the endothermic reaction Ca(OH)_2 de-hydroxylation occurs. The value is then multiplied by the molecular ratio $\text{Ca(OH)}_2/\text{H}_2\text{O}$ in order to obtain the amount of un-reacted calcium hydroxide.

TG-DTA Analysis condition

The thermal analyses have been performed with a heating rate of 10°C/min up to 1000/1100°C in air on a small quantity of powder, about 10 mg. STANTON 1500 STA and STA 409 (NETZSCH mod.) instruments were used.

All the MK powders and geopolymeric binders were analyzed.

2.2.2

Physical properties

2.2.2.1 X-Ray Powder Diffraction (XRD)

X-ray powder diffraction (XRD) is an analytical technique primarily used for phase identification of a crystalline material and can provide information on unit cell dimensions. The analyzed material is finely ground, homogenized and average bulk composition is determined.

X-ray diffraction is based on constructive interference of monochromatic X-rays and a crystalline sample. These X-rays are generated by a cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate and directed toward the sample. The interaction of the incident rays with the sample produces constructive interference (and a diffracted ray) when conditions satisfy Bragg's Law ($n\lambda = 2d \sin \theta$). This law relates the wavelength of electromagnetic radiation to the diffraction angle and the lattice spacing in a crystalline sample. These diffracted X-rays are then detected, processed and counted. By scanning the sample through a range of 2θ angles, all possible diffraction directions of the lattice should be attained due to the random orientation of the powdered material. Conversion of the diffraction peaks to d-spacings allows identification of the mineral because each mineral has a set of unique d-spacings. Typically, this is achieved by comparison of d-spacings with standard reference patterns.

X-ray powder diffraction is most widely used for the identification of unknown crystalline materials (e.g. minerals, inorganic compounds). identification of fine-grained

minerals such as clays and mixed layer clays that are difficult to determine optically, determination of unit cell dimensions, measurement of sample purity.

XRD can be also used to determine crystal structures using Rietveld refinement or determine modal amounts of minerals.

Experimental

About 0.5 g of fine powders (< 100 μm) was analyzed by using a BRUKER D8 ADVANCE diffractometer. Monochromatic CuK α radiation was employed. The X-ray scan was made over the 2θ range from 4 to 64°, with data acquisition at intervals of 0.02°. Crystalline phases were identified comparing them with standard reference patterns from the Powder Diffraction File maintained by the International Centre for diffraction Data (ICDD).

2.2.2.2 Specific Surface Area by BET analysis

By BET (Brunauer, Emmett and Teller) the specific surface area of a sample is measured, including the pore size distribution. This information is used to predict the dissolution rate, as this rate is proportional to the specific surface area. Thus, the surface area can be used to predict bioavailability. Further it is useful in evaluation of product performance and manufacturing consistency.

The specific surface area of a powder is determined by physical adsorption of a gas on the surface of the solid and by calculating the amount of adsorbate gas corresponding to a monomolecular layer on the surface. Physical adsorption results from relatively weak forces (van der Waals forces) between the adsorbate gas molecules and the adsorbent surface area of the test powder. The determination is usually carried out at the temperature of liquid nitrogen. The amount of gas adsorbed can be measured by a volumetric or continuous flow procedure.

Experimental

The specific surface area analysis was performed with a THERMO SCIENTIFIC, SURFER (BET) SRFA 14/008 Analyzer by using 0.5g of fine powders (<100 micron) dried at 200 °C for 1h

2.2.2.3 Particle size analysis

The particle size distribution of the powders is determined by exploiting the speed of sedimentation of the dispersed particles in a liquid medium according to Stokes 'law'.

The concentration of the different granulometric fractions is detected by determining the opacity of the window of the cell containing the suspension to the passage of a beam of rays X.

The analysis is performed during the sedimentation by scanning the cell, upwards along its vertical axis.

Coarser particles are detected first, since their sedimentation velocity is larger, while smaller ones require longer detection times due to their smaller sedimentation velocity.

To save measurement time, during the analysis the cell is moved downwards at a velocity determined according to Stokes' Law, which makes the determination of the finest particles faster.

Particle size influences many properties of particulate materials and is a valuable indicator of quality and performance of powders, suspensions, emulsions, and aerosols. The size and shape of grains influence flow and compaction properties of powders.

Experimental

The grain size distribution was obtained by using SEDIGRAPH III V1.01 Analyzer. About 100g of sieved (<100 micron) powder were used.

2.2.3

Microstructural properties

2.2.3.1 Scanning Electron Microscopy (SEM)

The SEM analysis is routinely used to generate high-resolution images of shapes of objects and to identify phases based on qualitative chemical analysis and/or crystalline structure

A typical SEM instrument, showing the electron column, sample chamber, EDS detector, electronics console, and visual display monitors. The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that derive from electron-sample interactions reveal information about the sample including external morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample, and a 2-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in

width can be imaged in a scanning mode using conventional SEM techniques. The SEM is also capable of performing analyses of selected point locations on the sample; this approach is especially useful in qualitatively or semi-quantitatively determining chemical compositions (using EDS), crystalline structure and crystal orientations (using EBSD).

Accelerated electrons in an SEM carry significant amounts of kinetic energy, and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), backscattered electrons (BSE), diffracted backscattered electrons (EBSD that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (cathodoluminescence—CL), and heat.

Secondary electrons and backscattered electrons are commonly used for imaging samples: secondary electrons are most valuable for showing morphology and topography on samples and backscattered electrons are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination).

X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, they yield X-rays that are of a fixed wavelength (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is "excited" by the electron beam. SEM analysis is considered to be "non-destructive"; that is, x-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

SEM always have at least one detector (usually a secondary electron detector) and most have additional detectors. The specific capabilities of a particular instrument are critically dependent on which detectors it accommodates.

Samples must be solid and they must fit into the microscope chamber. Maximum size in horizontal dimensions is usually on the order of 10 cm, vertical dimensions are generally much more limited and rarely exceed 40 mm. For most instruments samples must be stable in a vacuum on the order of 10^{-5} - 10^{-6} torr. Samples likely to outgas at low pressures (rocks saturated with hydrocarbons, "wet" samples such as coal, organic materials or swelling clays, and samples likely to decrepitate at low pressure) are

unsuitable for examination in conventional SEM's. However, "low vacuum" and "environmental" SEMs also exist, and many of these types of samples can be successfully examined in these specialized instruments.

Experimental

SEM observations were performed thanks to scanning electron microscope with field emission SEM-FEG [Zeiss, mod.Sigma (Zeiss NTS GmbH, Oberkochen, Germany)], and Scanning electron microscope FEI mod.Quanta200 ESEM (EIF-part of ThermoFisher Scientific Inc., Hillsboro, Oregon, USA)].

This analysis was used to determine the morphology of the MK grains and the microstructures of geopolymeric materials (binders and composites).

2.2.3.2 Micro X-Ray Tomography

X-ray microtomography (also frequently referred to as micro CT) is a radiographic imaging technique that can produce 3D images of a material's internal structure at a spatial resolution better than 1 micrometer. The specimen preparation is typically minimal, and for many materials the technique is nondestructive allowing many scans to be made of the same specimen under different conditions.

The technique is complementary to higher resolution 2D microscopy and lower resolution 3D ultrasonic imaging. While most early applications of computerized tomography were for medical imaging, the benefits of true three-dimensional maps of internal structure led to rapid adaptation of the technique in other fields, including materials science. Specialized industrial CT scanners were produced that were capable of imaging materials of greater density than human tissue.

Over the years, conventional CT scanners employed X-ray tube sources in which electrons are accelerated and allowed to collide with a target producing Bremsstrahlung radiation. Acquisition of 2D radiographs required appropriate scintillation, to convert the X-rays to visible light, and photodetectors to produce a digital image. Earlier CT scanners used a linear array of photodetectors, which meant tomographic slice images had to be acquired and reconstructed one plane at a time. Subsequent application of 2D detectors allowed the acquisition of 2D projection images leading to faster scan times. The spatial resolution of conventional CT systems is typically limited by the geometry of the X-ray beam along with the characteristics of the detector.

The spot size of the X-ray source plays an important role. The smaller the spot size, the smaller the penumbral blurring, which will help produce a more accurate the projected image. A larger spot size means that photons hitting a particular pixel can be traced back through different ray paths through the specimen. As detailed below, this adds significant noise to the tomographic reconstruction.

For this reason, commercial CT systems typically employ microfocus X-ray sources with spot sizes approaching a few micrometers or smaller. One megapixel detectors (e.g. 1024 by 1024) are routine, while some units boast 10+ megapixel detectors.

A significant development in microtomographic imaging was the use of synchrotron radiation as an X-ray source, which brought significant enhancements to the imaging that can be done. Synchrotron radiation results from the bending of a high-energy electron beam due to a magnetic field. The emitted light is many orders of magnitude greater in brightness than that emitted by conventional X-ray sources.

The implication for tomography is that the high flux allows one to resolve very subtle variations in absorptivity and therefore internal structure. The analog for this phenomenon could be the difference between taking a photograph in low light, where the resulting image can be grainy, and taking a photograph with an accompanying flash, where the resulting image has much higher contrast. Additional advantages of synchrotron radiation include X-ray beam collimation, which simplifies the tomographic reconstruction algorithm, and the tunability of the X-ray energy to a narrow energy band. As noted below, the use of a monochromatic X-ray beam improves the accuracy of the reconstructed tomographic images by eliminating the issue of energy dependence on X-ray absorption.

Sample's preparation and analysis conditions

The geopolymer samples (1x1x1 cm) were analyzed by a Micro-CT System equipped by an MicroFocus X-Ray source Kevex PXS10, 130kV (THERMO ELECTRON CORPORATION) coupled to a CCD X-Ray FDI VHR 1:1, KODAK KAI 11000. Resolution: Pixel size detector 0.018 mm, Voxel size reconstruction 0.009 mm.

2.2.3.3 Porosity analysis by Mercury Porosimetry

Mercury porosimetry uses the non-wetting properties of mercury to gain information on the porous characteristics of solid materials: porosity, pore volume, pore size distribution and density. During a typical porosity analysis in a mercury porosimetry

analyzer, a higher pressure is needed to force intrusion of mercury in smaller pores, whereas mercury intrusion in larger pores already occurs at low pressure. In this way a wide dynamic range of pore sizes can be measured and a pore size distribution can be obtained starting from 4 nm (pressure = 400 MPa) up to approx. 800 μm (vacuum). As a consequence, mercury porosimetry is extremely suitable for materials showing broad distributions of pore sizes or mainly macropores.

The typical result of a mercury porosimetry measurement comprises a graphical representation of the mercury intrusion curve and extrusion curve and the corresponding pore size distribution accompanied by data on pore volume, pore size, density and porosity.

Sample's preparation and analysis conditions

A fragment of geopolymers samples (max 10x10x10 mm) was analyzed by a Pascal 140 e Pascal 240 ThermoFinnigan Mercury Porosimetry.

2.2.4

Mechanical properties

The mechanical tests are performed with the purpose of measuring the mechanical properties of the materials, that is, their behavior under stress of external forces, and consequently their possible applications.

The choice of tests is carried out on the basis of the final application of the product and to its functionality. The mechanical properties differ according to the applied stress to the sample depending on the axis geometry - horizontal or vertical - affected by the load. The load exerted to test a mechanical resistance is of the static type, that is, through a slow and constant motion.

2.2.4.1 Compressive strength

Compressive strength or compression strength is the capacity of a material or structure to withstand loads tending to reduce size, as opposed to tensile strength, which withstands loads tending to elongate.

When a specimen of material is loaded in such a way that it extends it is said to be in tension. On the other hand, if the material compresses and shortens it is said to be in compression.

On an atomic level, the molecules or atoms are forced apart when in tension whereas in compression they are forced together. Since atoms in solids always try to find an equilibrium position, and distance between other atoms, forces arise throughout the entire material, which oppose either tension or compression. The phenomena prevailing on an atomic level are therefore similar.

By definition, the ultimate compressive strength of a material is that value of uniaxial compressive stress reached when the material fails completely.

Compressive strength is one of the most important engineering property of Concrete which designers are concerned of. It is a standard industrial practice that the concrete is classified based on grades. This grade is nothing but the Compressive Strength of the concrete cube or cylinder. Cube or Cylinder samples are usually tested under a compression-testing machine to obtain the compressive strength of concrete.

The goal of a compression test is to determine the behavior or response of a material while it experiences a compressive load by measuring fundamental variables, such as, strain, stress, and deformation. By testing a material in compression the compressive strength, yield strength, ultimate strength, elastic limit, and the elastic modulus among other parameters may all be determined.

Typically materials subjected to compression testing have a compressive strength generally accepted to be high and a tensile strength (e.g. tensile test) that is considered to be of a lower value. Almost all materials can experience compressive forces in one way or another depending upon their application, but the most common materials are composites, concretes, wood, stone, brick, mortars, grouts, polymers, plastics, foam and metals among many others.

Sample's preparation and analysis conditions

The test specimens were realized by following the indications shown in the standard UNI-EN12390-1. This requires that the height and base are in ratio 2:1 and the tolerance of the perpendicularity from the cylinder axis is more or less 0.5 mm. Initially cylindrical samples (14 mm in diameter and 28 mm in height) were produced,, and subsequently in form of parallelepiped with the dimensions of 10x10x20 mm.

For the compressive tests, the standard UNI-EN12390-3 used for the concretes has been applied and a Zwick/Roell Z050 universal testing machine was used.

2.2.4.2 Flexural strength

The bending test allows determining the breaking stress of brittle materials, that is, their point of maximum load. There are two types of bending tests: a "three-point" and "four points"; in both the load it is applied perpendicularly on the long side of the sample. The applied force increases steadily and the measurement is stopped as soon as the break occurs specimen.

A three-points bend test consists of the sample placed horizontally upon two points and the force applied to the top of the sample through a single point so that the sample is bent in the shape of a "V". A four-points bend test is roughly the same except that instead of the force applied through a single point on top it is applied through two points so that the sample experiences contact at four different points and is bent more in the shape of a "U".

The section of the specimen can be cylindrical, rectangular or square. The length is variable according to the material to be tested.

Generally a flexure test is run until the sample experiences failure and is therefore ideal for the testing of brittle materials. The most common materials tested in flexure are plastic materials, composites, concrete, and ceramics. Because these materials have a very low ductility they will break before any permanent deformation of the sample occurs allowing for the accurate measurement of the flexural modulus and strength.

Sample's preparation and analysis conditions

The test specimens have been realized by following the indications shown in the standard UNI-EN12390-5 (used for the concretes) while the UNI-EN843-1 (used for determining the flexural strength of monolithic ceramics at room temperature), have been utilized for the flexural test. Samples were produced with parallelepiped shape of 10x10x45 mm. A Zwick/Roell Z050 universal testing machine was used.

Chapter 3

Geopolymeric binders

3.1

Introduction

The selection and the characterization of raw materials are basic in the production of geopolymeric binders with good stability from chemical, physical and mechanical point of view. The main function of the binder is to bond more or less reactive aggregates and/or fillers with different particles size, surface area and porosity. A good binder should maintain its binding capacity (or “cementing ability”) in different environmental conditions and during the time. For this reason particular attention was given to this theme.

In this chapter the results of characterization of raw materials, the formulation of geopolymeric binder and the characterization of final product are presented.

3.2

Experimental procedures

3.2.1 Materials and methods

Commercial Kaolins identified as BS4 and BS6 (Petra-Minerals and Imerys Kaolin, France) were used to prepare geopolimers for this PhD study.

First of all, they were characterized and adequately prepared through amorphization processes (see Chapter 2).

For both metakaolins (MKs) the calcination processes were carried out in the CNR-ISTEC laboratories (Faenza), in an electric kiln with a heating gradient of 200°C/h, until 650°C, a soaking time of 2 h and a natural cooling inside the kiln. These parameters were selected on the basis of a previous CNR-ISTEC study [77].

The mechano-chemical treatments (only for the BS4) were carried out in the CNR-IMC/IGAG laboratories (Rome). BS4 was grinded under different conditions and times: from 9 to 60 minutes using two different speeds (900 and 1500 rpm) and different ratios between the moving mass and the grinded material ($M/m=250$ and $M/m=120$). In this

PhD thesis only "13, 18 and 30 minutes" at 1500 rpm and M/m=120 were? taken into consideration.

Alkaline solutions were prepared by dissolving KOH pellets (85%, Sigma-Aldrich, Germany) into potassium silicate solutions (Ingessil S.r.l, Italy).

The ratios for the formulation of the binders were selected on the bases of the MKs chemical compositions in order to achieve the following molar ratios: $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.6$; $\text{M}_2\text{O}/\text{Al}_2\text{O}_3 = 1$; $\text{H}_2\text{O}:\text{K}_2\text{O} = 5-12$.

These values were maintained constant for the two types of MKs. According to the different level of amorphization the formulations were changed considering the amount of reactive Al. This last measured by NMR spectroscopy and pozzolanic activity is 90-85% for the BS4 activated by mechano-chemical process and 75% for the BS4 and BS6 activated by thermal treatment.

Generally $\text{H}_2\text{O}/\text{K}_2\text{O}$ ratios were chosen "a posteriori" on the basis of the different workability of the mixtures.

The Kaolins and MKs obtained under grinding conditions and thermal process were characterized by using different analytical techniques. In addition, specific tests to assess other properties as mechanical performances and physical aspects were performed on the geopolymeric binders.

All these analytical techniques and their working conditions applied are described in Chapter 2.

3.2.1.1 Kaolins and metakaolins characterization

X-ray Fluorescence (XRF) and X-ray Powder Diffraction (XRPD) were used to determine the chemical and mineralogical compositions of kaolin powders, respectively. XRD permitted to verify the transformation of clayey minerals, more precisely kaolinite into amorphous and so reactive phases. Particles size distribution and specific surface area by BET method were used to evaluate the reactive properties, while Scanning Electron Microscope (SEM) to observe the morphology of the grains.

Thermal analyses (TGA/DTA) were used to detect and to quantify the thermo-labile crystalline phases present in kaolin powder, and to control the complete

dehydroxylation of metakaolinite and gibbsite. As regards the MK TGA and DTA permitted to verify the “pozzolanic capacity”.

Coordination number of Aluminum by ^{27}Al MAS NMR spectroscopy were used to verify and quantify the presence of reactive Al (V and IV).

3.2.1.2 Geopolymeric binders characterization

As mentioned above, binders were characterized with some of the analytical techniques used for the raw materials. In particular: MAS NMR spectroscopy were used to verify the presence of Al(IV) as geopolymerization indicator, TGA/DTA to control the dehydroxylation of the materials, SEM observations to determine the morphological features, porosity and flaws of the binders.

In addition other tests were used in order to determine chemical, physical and microstructural properties.

- More precisely, NMR Relaxometry was used to follow the content of water and how it changes over time and to get information about time geopolymerization and kinetic process,
- FTIR spectrometry was used to verify the formation of specific molecular bonds
- Mercury Intrusion Porosimetry (MPI) was used to assess differences in porosity and density,
- Micro Computed Tomography was used for obtain information about bulk microstructure without any mechanical stress,
- Mechanical tests (adhesion capacity, uniaxial compression and flexural strength) were used to assess the mechanical resistance of materials after their integration as structural elements in building or restoration fields.

3.2.2 Geopolymer's synthesis

A calculated quantity of potassium silicate aqueous solution was put into a becker together with a calculated amount of potassium hydroxide pellets. The mixing developed an exothermal reaction, so that to facilitate its cooling the becker was put into a container with cold water.. Successively a weighted quantity of the metakaolin powder was added and mixed by using a mechanical mixer for 2-5 minutes (figures 1-2).

If necessary, a weighted quantity of distilled water was added in order to obtain a mixture suitable to be poured.

The obtained mixture was poured into plastic or silicone molds (depending on the required shape, in particular for mechanical tests) in order to prepare several samples for each mixture, finally sealed with *Parafilm*.

Samples were cured at room temperature for 24h and then in oven at 60°C for 24h to facilitate the dehydration process. After this time, the samples were removed from the molds and preserved into sealed envelopes for permitting an homogeneous and gradual drying.

After the “curing time” (generally 28 days at room temperature) the samples were analyzed as reported above.

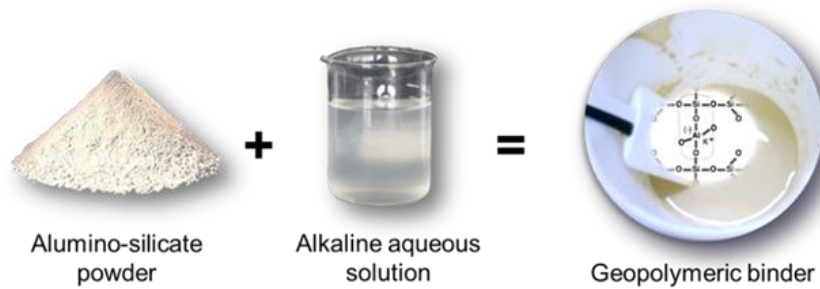


Fig. 1 Schematic procedure to produce the geopolymer binder



Figures 2 (a-e). Examples of mixing and pouring the geopolymeric binders

3.3

Results and discussion

3.3.1 Raw materials

3.3.1.1 Chemical composition

Chemical compositions performed by XRF analysis of BS4 and BS6 kaolins are reported in table 1, while table 2 shows their particles size values (Φ 50) and the specific surface area compared to metakaolins precursors treated by heating.

It is possible to note that in spite of their chemical composition very similar, other physical properties (important from a rheological point of view) can vary greatly.

In fact, the BS6 which is characterized by a lower grain size distribution and consequently by a higher specific surface area has proven to be more reactive in response to calcination.

This aspect can be deduced by the color variation: in fact, starting from light gray kaolins a MK BS4 beige in color and a MK BS6 light pink in color were obtained. This can be probably due to the greater oxidation of ferrous components (that are quantitative the same).

Kaolin	Chemical composition (wt %)									
	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	K ₂ O	Na ₂ O	CaO	MgO	P ₂ O ₅	LOI
BS4	43.02	37.24	1.00	0.96	0.55	0.03	0.11	0.01	0.01	16.98
BS6	43,18	38,49	1,17	1,05	0,36	0,00	0,15	0,01	0,05	14,03

Table 1: Bulk composition (wt. %) and loss on ignition of BS4 and BS6 kaolins

Sample	SSA (m ² /g)	Particle size (Φ 50- μ m)
BS4	18.0	1.3
BS4 MK-T 650°C	27.5	4.4
BS6	22,3	0.3
BS6 MK-T 650°C	35.6	1.6

Table 2: Grain size and SSA of BS4 and BS6 kaolins and derived metakaolins

3.3.1.2 Granulometric parameters

Regarding the BS4, in order to better understand some of reactivity phenomena due to the different amorphization processes, a more detailed study of the particle size distribution were performed and reported in table 3.

Sample	Φ_{50} (μm)	Sand (%)	Silt (%)	clay (%)	> 20 μm (%)	2-20 μm (%)	< 2 μm (%)
BS4 Kaolin	1.3	1.8	27.2	71	9	32	59
BS4 MK-T 650°C	4.4	4.5	45.5	50	17	50	33
BS4 MK-M 13'	6.3	4.5	55.5	40	24	49	27
BS4 MK-M 18'	5.5	2.5	54.5	43	21	49	30
BS4 MK-M 30'	4.5	3.2	49.8	47	20	46	34

Table 3 – Granulometric parameters: Sand = > 63 μm ; silt = 4-63 μm ; clay = < 2 μm

These data, the average diameter of the grains ($\Phi 50$), the percentages and the distribution of the particles, show how the two amorphization treatments can affect the capacity of aggregation of particles, leading to an increase in their size both in thermal that in mechano-chemical processes.

In fact, the raw kaolin is characterized by very fine particles as demonstrated by the value of $\Phi 50$ that is 1.3 micron.

After thermal and mechano-chemical treatments, the particles become bigger. It means that an aggregation process develops during the treatment. As regards the thermal treatment the new value of average diameter is 4.47 micron. A dimensional variation mainly involves the finest particles; their percentage (<1micron) decreases from 44% to 16%.

A similar process happens in the particles of the powders obtained by mechano-chemical treatments at different time of grinding. But some points are necessary to clarify. This type of activation provokes an increasing of silty fraction proceeding with the treatments. By increasing the grinding time, the resulting powders show a behavior similar to those of meta-kaolin, at least in particular for the range of values comprised between 10-2 microns. Under 2 micron the behavior is quite different; the metakaolin is characterized by less amount of clayey particles in comparison with the grinding kaolins. If we consider the curves relative to the minor grinding times, it can note a drastically decrease of the silty fraction, so the major times of grinding causes an rearrangement of the packaging of the finest particles for forming “coarser” particles.

3.3.1.3 Macroscopic and microscopic aspects

As mentioned above, an interesting aspect concerns the color of MKs powders. It was possible to get different colors, not only from two different kaolin, but also from the same kaolin.

While the thermal process has given a light beige BS4 MK-T, the mechano-chemical has been transformed the initial kaolin into a gray “smoke” powder similar to the Portland cement (Figure 3).

This aspect is particularly evident during the powders hydration (Figures 2 a-e) and taking into account the application field, e.g. Cultural Heritage, it is not to be underestimated.

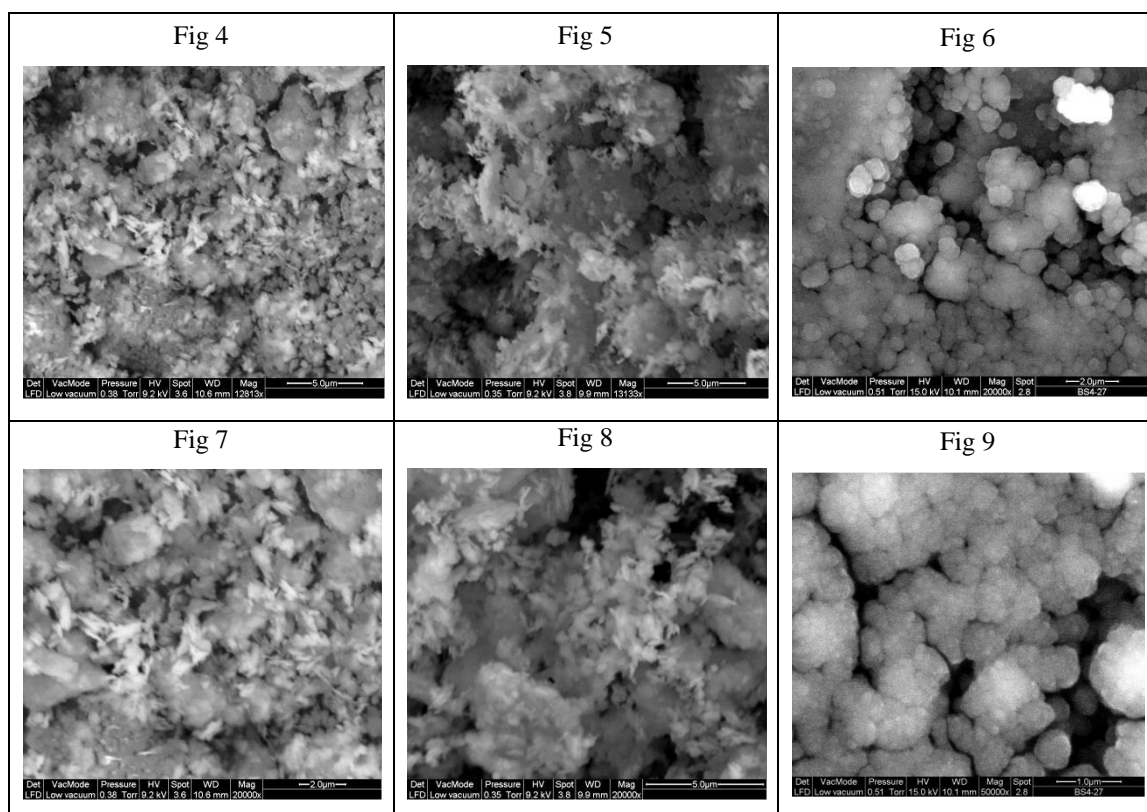


Figure 3. Comparison between BS4 kaolin and metakaolin powders

With regard to the morphology of the particles of MKs SEM observations confirmed that the amorphization treatment, also influences the microstructure.

MKs -T (BS4 and BS6) maintain the typical lamellar structure of the precursor kaolin. On the contrary, the MK-M (for all grinding times) is characterized by globular particles, rounded, which tend to aggregate, appearing at macroscopic level a more coarse powder, similar, also in this case at Portland cement (Figures 4-9)

BS4 Kaolin	BS4 MK-T 650°C	BS4 MK-M (13', 18', 30')
Fig 8	Fig 9	Fig 10



Figures 4-9. SEM Images of kaolin and metakaolin powders

The differences between them, as shown in Table 2, are the lower grain size of the particles..

3.3.1.4 NMR analysis

The ^{27}Al MAS NMR analysis was carried out to monitor the change of coordination number of Al in the thermally treated BS6 and in the mechano-chemically treated BS4. Previous study carried out on the reactive capacity of the MK BS4 calcined at 650°C has permitted to define the "right degree" of amorphization of the material.

The NMR analysis revealed that a kaolin as the BS6, with chemical and mineralogical composition similar to BS4, treated with the same thermal condition can produce a transformation of the Al coordination identical to BS4 (Figure 10).

However, as regards the mechano-chemical process, where the material has been observed after different steps, it was noted that after just 18 minutes of grinding is possible to obtain a ^{27}Al MAS NMR spectrum comparable with that of MK BS4 obtained by thermal treatment (figures 11).

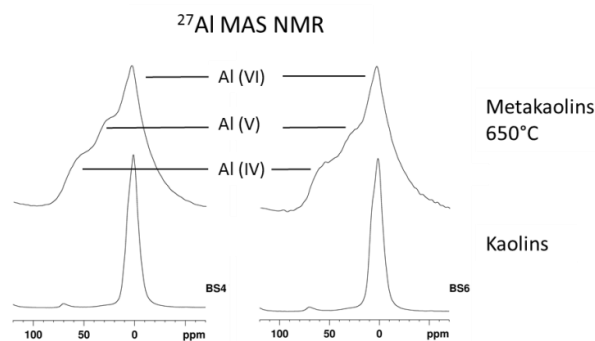


Figure 10. Comparison between BS4 and BS6 kaolins and derived calcined metakaolins

For the different grinding times the values of Al (V) can also be observed, which seemed to increase in proportion to the time of grinding. These values were very useful to choose the most suitable powders for the production of geopolymers.

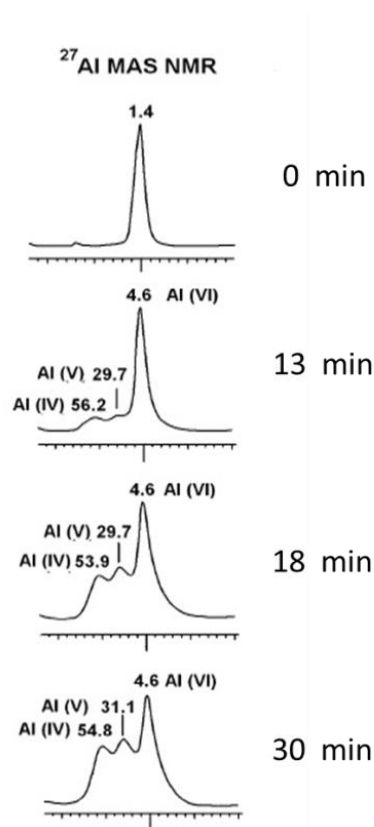


Figure 11. NMR spectra of BS4 untrated and after 13, 18 and 30 minutes of grinding

Another interesting aspect is that the mechano-chemical process acts not only on the Al stability, but also on that of the other components such as silicon (detailes are not reported in this PhD thesis).

For this reason, the amount of reactive Al calculated for mechano-chemical MK-BS4 was 85-90%, while for thermal treated about 75%.

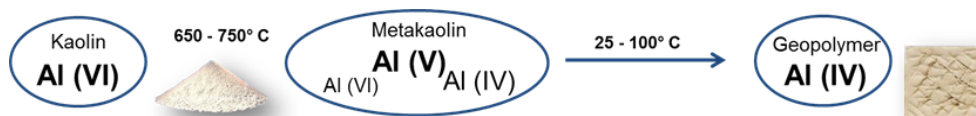


Figure 12. Schematic change of kaolin coordination

3.3.1.5 FTIR analysis

FTIR (Figure 13) spectra assess the progressive conversion of Kaolin into Metakaolin; structural changes are caused by dehydration of the -Al-OH present in Kaolin. Kaolin profile shows that many vibrational -Al-OH bands are present and they are well separated by those of Gibbsite. The metakaolin spectrum shows an increase of Si-O/Al-O bands in the range of 1000-600 cm⁻¹. This behavior can be seen for both the MK-T and MK-M.

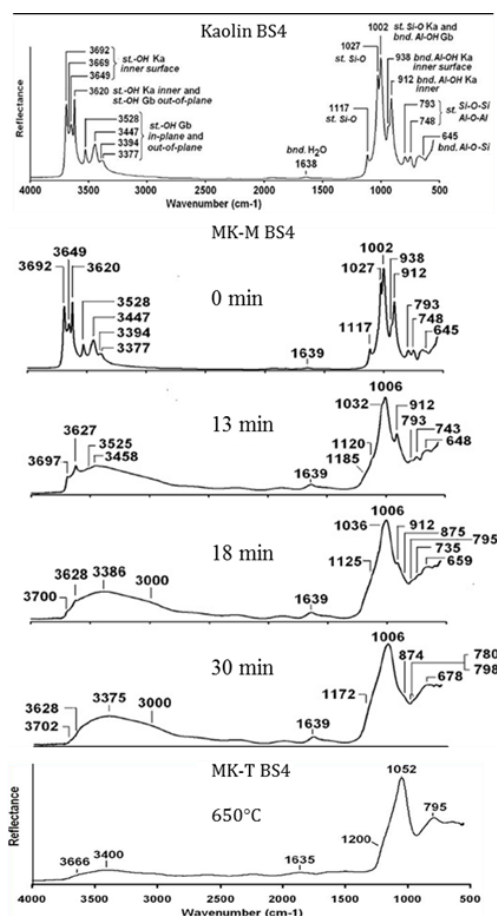


Figure 13. Kaolin BS4 and MKs BS4 spectra

3.3.1.6 XRD analysis

XRD spectrum of Kaolin BS4, reported in figure 14a, shows the presence of kaolinite and gibbsite, and also quartz and illite as mineral phases. Figure 14b shows the amorphous structure typical of metakaolin after thermal treatment, that means metakaolin.

In Figure 15 are reported XRD spectra of MKs-BS4 after thermal and mechanochemical treatments. It is possible to note that only in MK-T, quartz, illite and a very small quantity of anatase are still present.

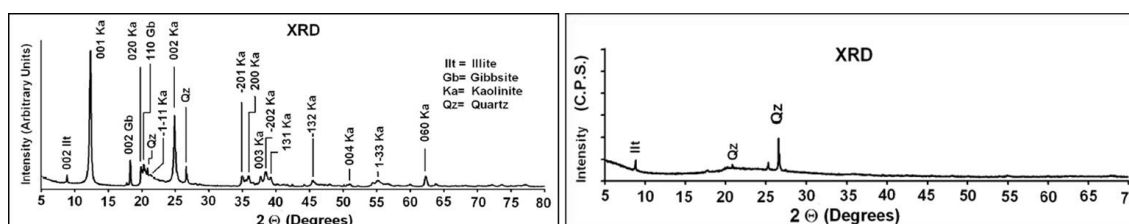


Figure 14. XRD spectra of kaolin BS4 (a) and MK-T BS4 (b)

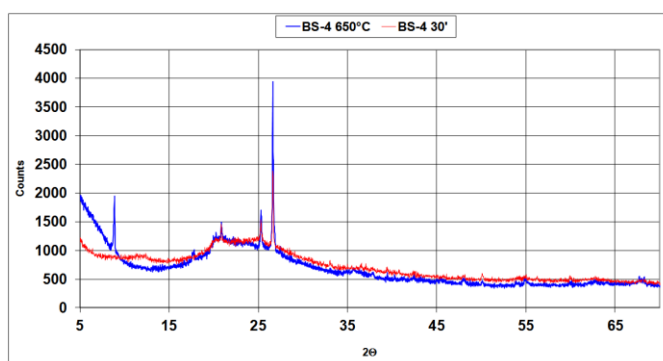


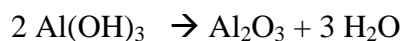
Figure 15. Comparison between XRD spectra of MK-T BS4 (red) and MK-M BS4 (blue)

3.3.1.7 Thermal analysis

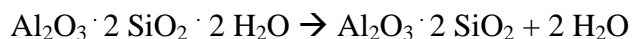
BS4 and BS6 kaolins were also analyzed by TGA-DTA.

The DTA curve of BS4 kaolin (Figure 16) shows three endothermic peaks and an exothermic peak: the first endothermic peak, around 100 ° C, is attributable to the release of water adsorbed in the pores and on the surface of the sample and the loss of the “zeolite water” (present in the interlayers of kaolinite).

The second endothermic peak, around 250 ° C is probably due to decomposition of hydroxides such as gibbsite (aluminum hydroxide) according to the reaction:



The presence of this endothermic reaction depends on the clay's purity; consequently this transformation may not be present, in general, in all kaolins. The third endothermic peak is mainly attributable to the dehydroxylation of the kaolinite and successively formation of metakaolinite according to the reaction:



This reaction takes place generally in the range 450-700 ° C; in some cases the peak has a shoulder, probably attributable to a pre-dehydroxylation or to the presence of illite in the sample.

The exothermic peak at temperatures above 900 ° C can be correlated to the γ -alumina formation.

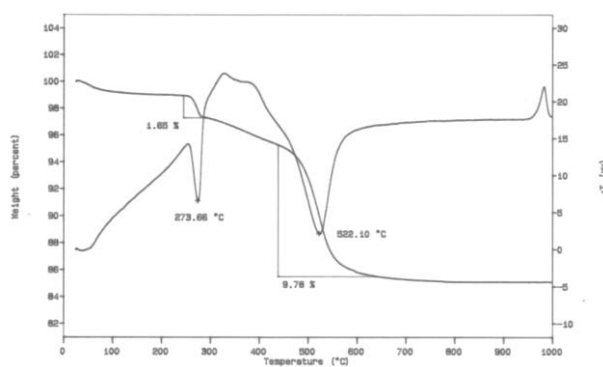


Figure 16. TGA/DTA relativa al caolino BS4

The progressive transition of Kaolin into Metakaolin can be also confirmed by TGA analysis providing information on the relative amounts of “hydroxyl groups” and water present in the kaolin. The major BS4 weight losses arise from endothermic dehydration of Gibbsite and Kaolinite, taking place, as reported, at 250 and 550°C, respectively .

Figures 17-20 report TG profiles of MKs taken into consideration in this PhD study.

It is interesting to note that in MK-T650 the weight loss attributable to “zeolitic water” (interlayer of kaolinite) is significantly lower compared to those of mechano-chemical MKs. It is also interesting to note that for grinding times of 13 minutes, a small weight loss attributable to kaolinite is still recognizable. On the contrary in the 18’ and 30’ powder no endothermic reactions are visible, but only the exothermic peak of alumina formation.

Fig. 17

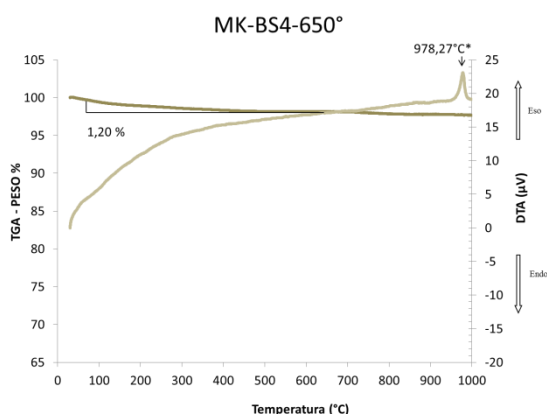


Fig. 18

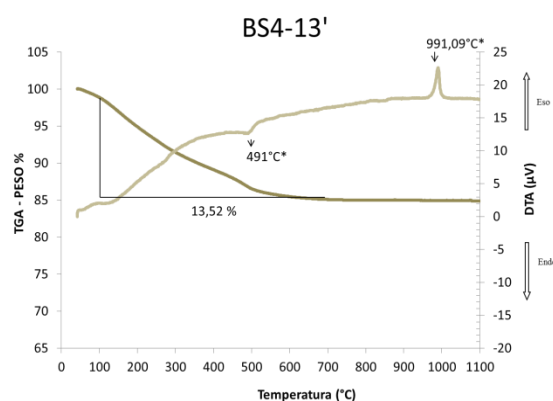


Fig. 19

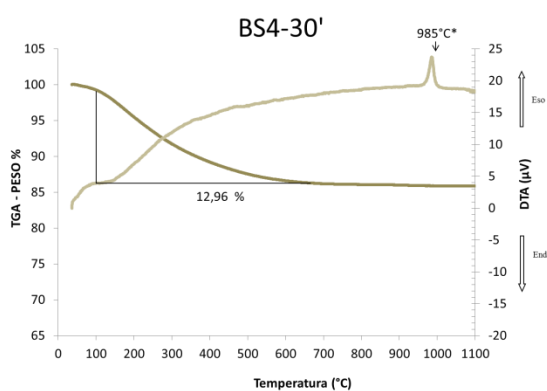
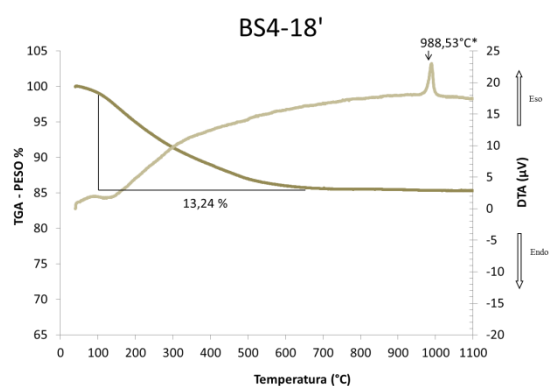


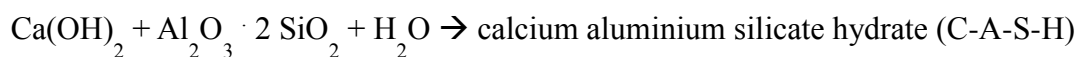
Fig. 20



Figures 17-20. TG profiles of dehydroxylated MKs

The main use of the thermal results is for evaluating the pozzolanic activity of metakaolin. This is very useful to verify the reactivity of the materials also during the geopolymerization process.

The metakaolin samples react with calcium hydroxide powder according to the reaction:



The procedure (modified Chapelle test) provides the mixing of Metakaolin 50% and 50% Ca (OH)₂ (by weight) into sealed tubes, and their preservation for 28 days at room temperature.

Every seven days a sample was dried and analyzed by TGA-DTA and the pozzolanic activity of the metakaolins was evaluated by determining the amount of Ca (OH)₂ residue.

In figures 21-30 and in table 4 are shown the results of the MKs previously reported, that are MKBS4650T, MKBS413', MKBS418', MKBS430' and MKBS6-650.

Fig. 21

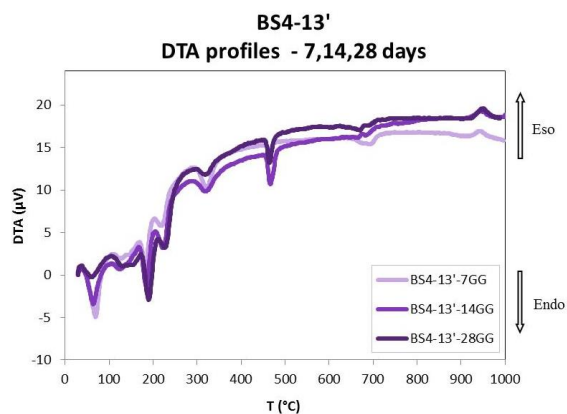


Fig. 22

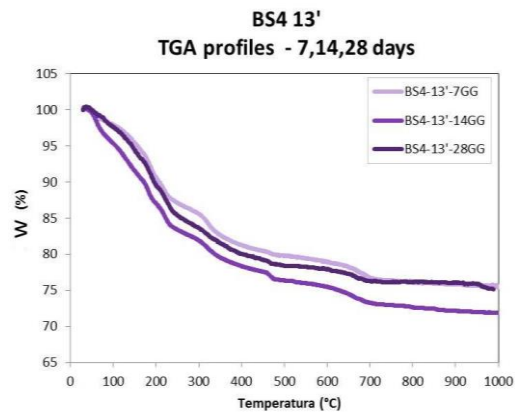


Fig. 23

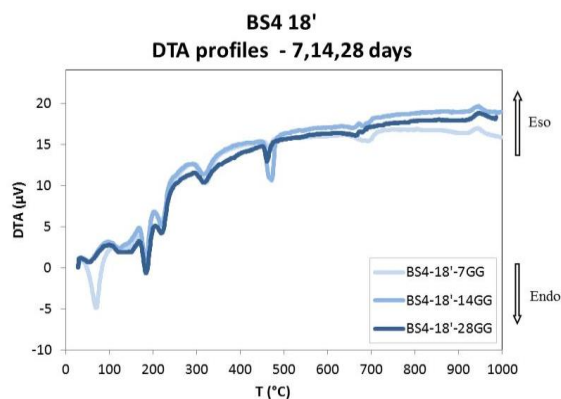


Fig. 24

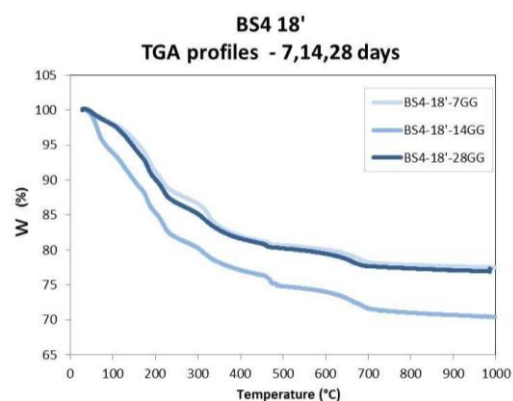


Fig. 25

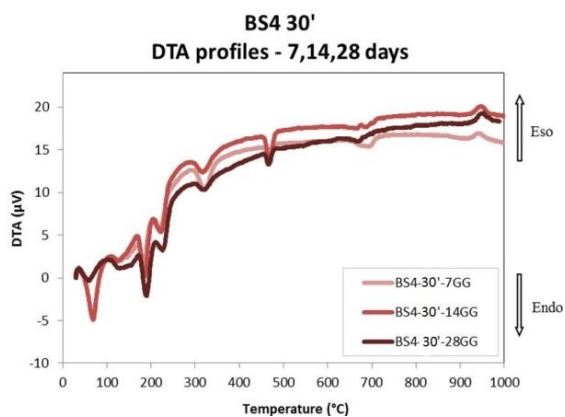


Fig. 26

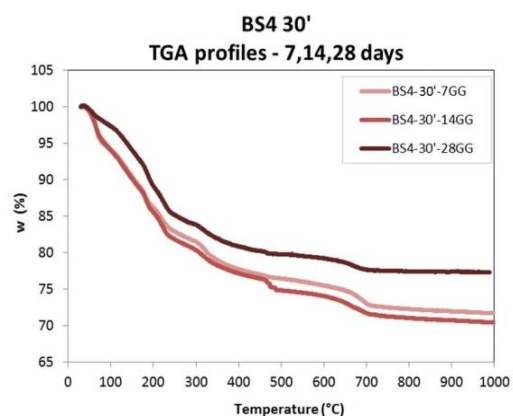


Fig. 27

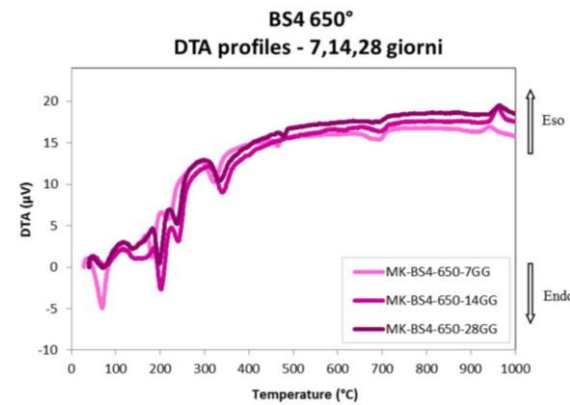


Fig. 28

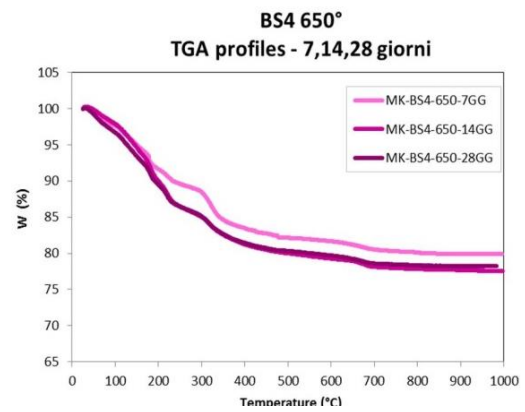


Fig. 29

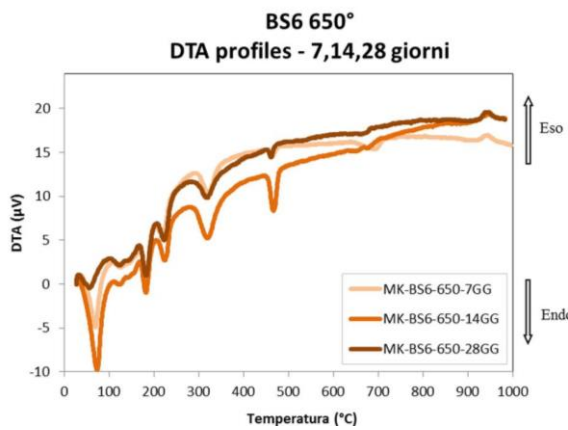
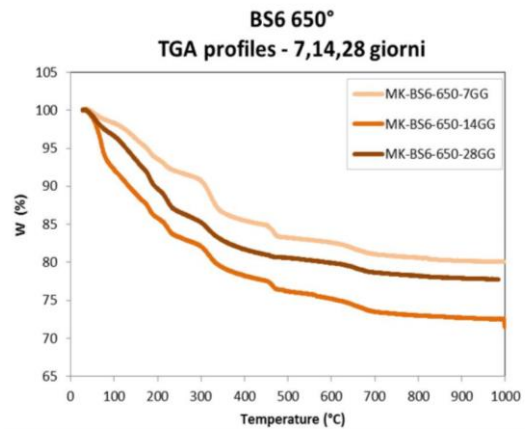


Fig. 30



Figures 27-36. TG profiles of MKs after pozzolanic reaction with calcium hydroxide

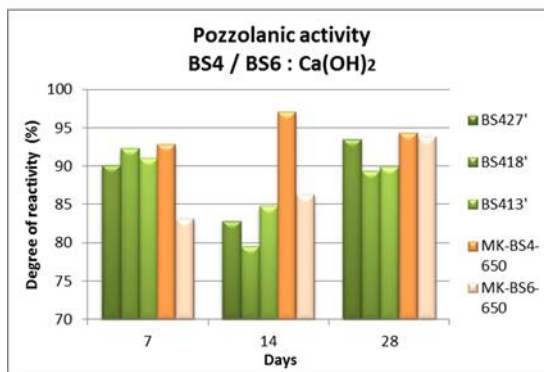


Figure 31.

Comparison between MKs pozzolanic activity expressed in % evaluated by the amount of Ca(OH)₂ residue

Sample/days	7	14	28
BS4-30'	90,12 %	82,87 %	93,45 %
BS4-18'	92,34 %	79,58 %	89,36 %
BS4-13'	91,06 %	84,79 %	89,91 %
BS4-650	92,87 %	97,10 %	94,44 %
BS6-650	83,14 %	86,37 %	93,85 %

Table 4.

Comparison between MKs pozzolanic activity expressed in % evaluated by the amount of Ca(OH)₂ residue

The percentages of reactivity of all MKs taken into consideration show that already after 7 days the consumption of calcium hydroxide is almost complete, that means that the reaction occurs.

After 14 days (except for the MK-T BS4) the reactivity percentage decreases and then up to the achievement of the 28 days of curing. This phenomenon is still not well understood, it may arise from the formation of new phases of C.A.S.H. that they are not totally stable and then disappeared. On the basis of all the data obtained it were possible to select the most suitable raw materials for the realization of geopolymers: MK-T BS4, BS6-MK-T and MK-M 30'. In particular, the analysis through ^{27}Al MAS NMR and TG described excellent reactivity profiles of these MK powders.

3.3.2 Geopolymers characterization

Sample	MK treatment	% Al reactive	Molar Ratios
GEO-BS4-650	Thermal	75	$\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.6$ $\text{M}_2\text{O}/\text{Al}_2\text{O}_3 = 1$ $\text{H}_2\text{O}/\text{K}_2\text{O} = 5-18$
GEO-BS4-30' _90	Mechano-chemical	90	$\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.6$ $\text{M}_2\text{O}/\text{Al}_2\text{O}_3 = 1$ $\text{H}_2\text{O}/\text{K}_2\text{O} = 5-18$
GEO-BS4-30' _85	Mechano-chemical	85	$\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.6$ $\text{M}_2\text{O}/\text{Al}_2\text{O}_3 = 1$ $\text{H}_2\text{O}/\text{K}_2\text{O} = 5-18$
GEO-BS6-650	Thermal	75	$\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.6$ $\text{M}_2\text{O}/\text{Al}_2\text{O}_3 = 1$ $\text{H}_2\text{O}/\text{K}_2\text{O} = 5-18$

Table 5. Molar ratios of geopolymeric binders

As described in 3.2.2, geopolymers were characterized by different analytical techniques in order to obtain information about the efficacy of geopolymerization.

3.3.2.1 NMR characterization

The most important chemical characterization was carried out by NMR. The ^{27}Al MAS NMR analysis (figure 29) demonstrates that, at the end of geopolymerization process Al is located almost entirely in (IV) coordination, according to the theory.

This data would indicate that the entire Al considered reactive actually reacted. Unfortunately the amorphous structure of the products obtained does not permit to carry out diffraction analysis to evaluate the formation of new phases.

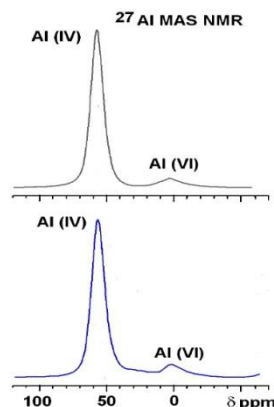


Figure 32. ^{27}Al MAS NMR of GEO-BS4-650 (black) compared to GEO-BS4-30' _85

Regarding the kinetics of reaction, different analytical techniques were used in order to follow the material geopolymerization material over the time.

Unfortunately, no significant results were obtained by using traditional analytical techniques (as FTIR or TG) because they are not sufficient sensitive and do not permit to follow the polymerization in "live" or "on line".

These techniques are reported below but results will not be discussed in this thesis:

- ^{27}Al MAS-NMR as mentioned above, showed the presence of tetrahedral Al nanocrystals and the presence of Al(VI) from unreacted metakaolin, that usually disappears over time,
- ^1H MAS-NMR: the proton NMR profile indicated that more $-\text{OH}$ in form of water or linked to the Si, Al structure were present, in particular in the «mechano-chemically» geopolymeric binder, but further studies are needed to understand the molecular structure,
- FTIR: negligible differences are in the spectra (collected from 1 to 120 minutes) of geopolymeric binders prepared with or without ethyl alcohol (in order to speed the dehydration and then the reaction process),
- TGA-DTA: negligible differences are in the spectra (collected from 1 to 120 minutes) of geopolymeric binders prepared with or without ethyl alcohol
- RAMAN analysis is not possible (due to the fluorescence phenomenon)
- XRD: geopolymer structure is nano-crystalline/amorphous and using traditional equipment was not possible to verify the presence of new nano-phases.

The only analytical technique, unfortunately used only recently, has provided interesting preliminary results regarding the kinetics of geopolymerization two types of geopolymer: ^1H NMR Time Domain-Relaxometry.

Geopolymerization kinetics of the compound produced from MK-T BS6 powder + alkaline solution (KSiI + KOH) was monitored by a study of the longitudinal relaxation times T_1 s and transverse relaxation times T_2 s of ^1H nuclei.

Measurements were executed as reported in Chap 2 and the process was monitored from 15 minutes to 15 days from the preparation.

The analysis of relaxation times distributions during the geopolymerization process allowed distinguishing different condition of restriction/trapping of ^1H .

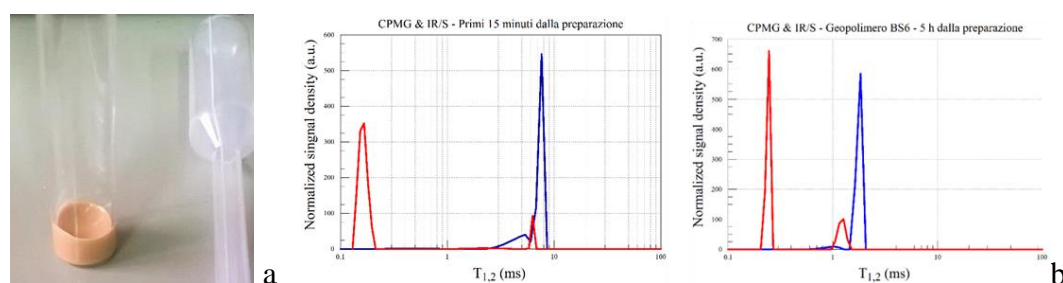


Figure 33. 33a: geopolymeric sample in the glass tube after analysis; 39b: ^1H nuclei signals after 15 minutes and 5 hours to sample preparation.

Results (Figure 33) suggest the presence of two different components:

the first, characterized by the shortest T_2 s and a T_1/T_2 ratio about 10, indicates the presence of ^1H in a liquid-solid state (presumably water molecules between Al-Si layer). The second is characterized by a T_1/T_2 ratio about 1, that indicates ^1H in fluid state, and it is ascribable to water molecules trapped in porous spaces of the order of micro-nano meters. During the geopolymerization, the T_2 of this second component decreases until reaches a transverse relaxation time similar to the first component (Figure 34).

So we can assume that a part of the hydrogenated fluid is used for the polymerization process (slowest component that converges to the fastest one) and the rest was expelled by evaporation. Of course, in the future more analysis will be necessary in order to confirm these data, now it was only possible to ensure that the technique was able to detect changes in the material during the reaction process.

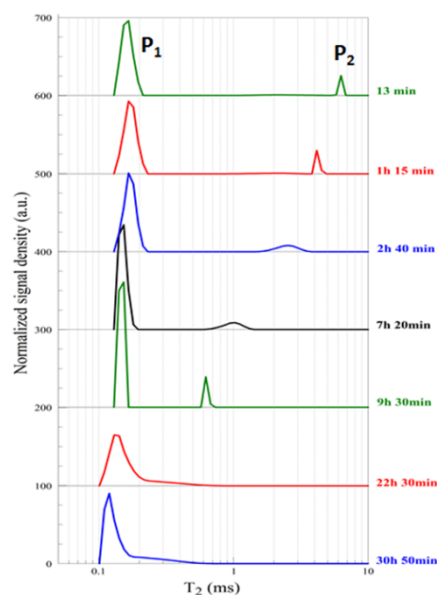


Figure 34. Decreased of T2 signal until reaches a transverse relaxation time similar to the first component

3.3.2.2 FTIR analysis

FTIR analysis doesn't have produced interesting information about kinetics of geopolymerization but it was possible to verify the effectiveness of geopolymerization through the comparison of the FTIR profiles with data reported in literature. Figure 35 shows the typical "pattern" of the peaks corresponding to the molecular bond present in the final geopolymeric structure. This pattern is present in all the samples produced with metakaolin thermally and mechano-chemical treated (table 6).

Wavenumber (cm-1)	Assigment [92, 93*]
3600-3100	O-H (stretching vibration-hydrogen bond, free water)
1650	O-H (hydrogen bond, free water/adsorbed atmospheric water)
1530	C-O (from potassium carbonate)*
1395	C-O (from potassium carbonate)*
1080-1100	Si-O (stretching vibration)
1008	Si (Al)-O (stretching vibration)
914	Al-OH (6 coordinated-stretching vibration)
694	Si-O (stretching vibration)
540	Si-O-Al (bending vibration)

Table 6. IR Characteristics vibration bands of "BS4 and BS6" geopolymeric binders

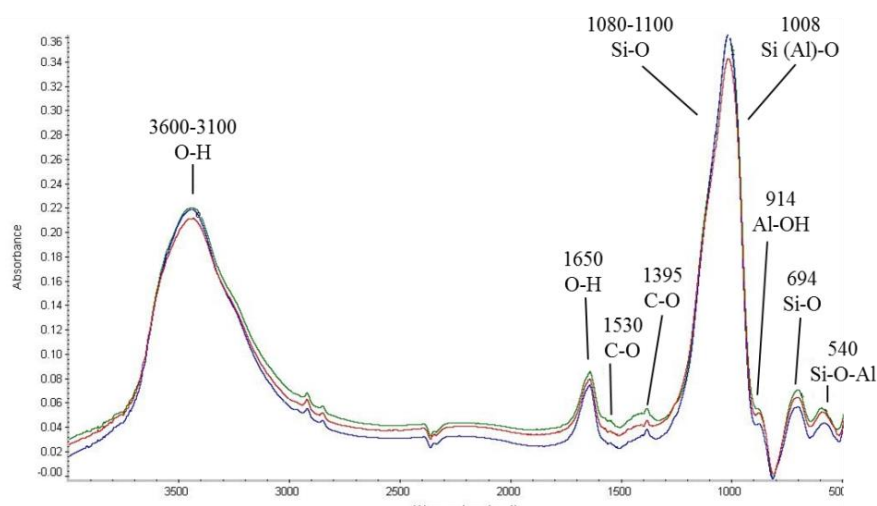


Figure 35. FTIR spectra of “BS4 and BS6” geopolymeric binders: GEO-BS4-30'_85 (green), GEO-BS4-650 (red) and GEO-BS6-650 (blue)

The presence of many -OH groups, such as free water, but also bound to Al (peak= 914 cm⁻¹, in small quantities), show that the final material maintains in its structure a percentage of water / -OH otherwise related.

This aspect may be due to the curing process (<100 °) or even to the presence of Al (VI) present in the MK not fully reacted that could trap the hydroxyl groups in its structure.

Another interesting aspect is that although different raw materials were used, the FTIR spectra are the same. Also in this case a more detailed study are necessary to better understand if these results derived to “instrumental limitation” or if really geopolymerization occurs in the same way when similar MKs were used.

3.3.2.3 Thermal analysis

The thermogravimetric analysis performed on geopolymeric binders showed that the material is constituted by a structure almost completely de-hydroxylated (450-550°) but with a significant presence of “hydration water” (peak around 100 ° C), probably attributable to the interlayer water and the presence of -OH groups (170-190 °) weakly bound.

These results confirm those obtained by FTIR previously presented. Figures 36-38 show the thermograms of 3 samples based on BS4 kaolin: GEO-BS4-650, GEO-BS4-30'_90 and GEO-BS4-30'_85.

GEO-BS4-650

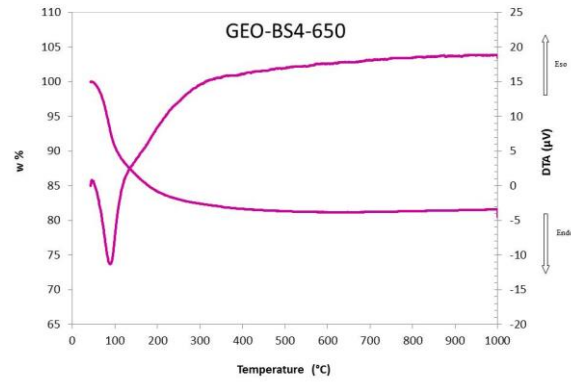


Fig. 36

GEO-BS4-30'_90

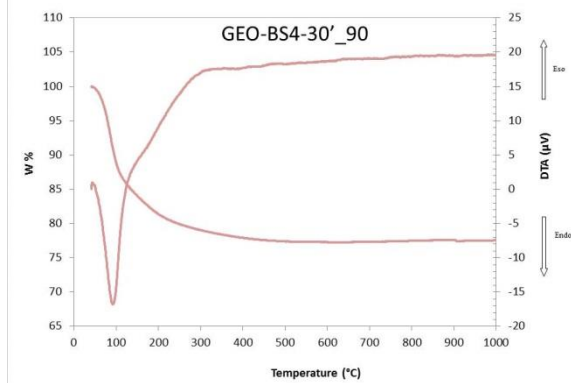


Fig. 37

GEO-BS4-30'_85

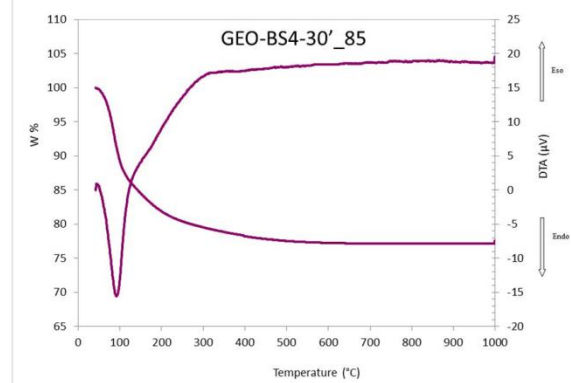


Fig. 38

Figures 36-38. TG profiles of geopolymeric binders based on BS4

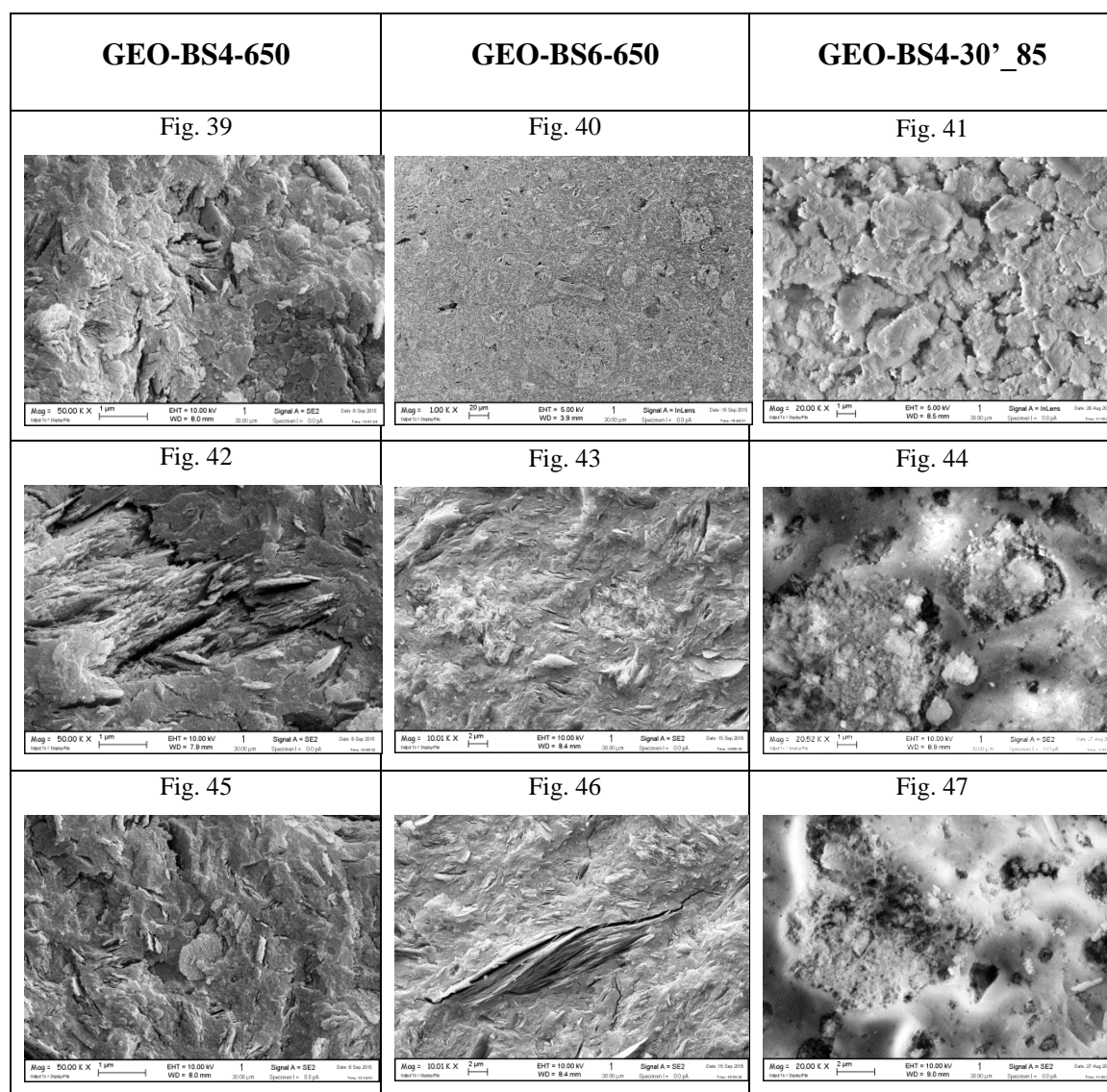
3.3.2.4 SEM observation

Microstructural study of binders was performed by SEM observations.

SEM observations are very important in order to study geopolymers microstructure in term of homogeneity, presence of microfractures, porosity, etc...

Some micrographs are reported below (Figures 39-47). In general all binders show a compact structure, characterized by the presence of the precursor metakaolin. In fact,

binders with BS4 and BS6 treated by thermal process maintain in their microstructures the typical lamellae that (unfortunately) in some case are also present “as packet structure”. This aspect can be derived from a too short mixing, which did not allow a total fragmentation/mixing of raw material, they could be considered of defect areas, in which the matrix presents a “discontinuity” affecting the mechanical strength of the final product. Also in the case of the binders derived by MK mechano-chemical activated, their structure reflects that of the starting powder; this matrix is characterized by a lesser compactness and very porous microstructure.



Figures 39-47. SEM images of geopolymeric binders derived by BS4 and BS6 metakaolins

3.3.2.5 Micro CT

In addition to the SEM analysis, Micro CT was used to study the microstructures.

The results obtained show that the internal structure does not seem affected by microfractures of large dimensions at least with respect to the detection limit.

Because the technique is based on the different absorption capacity of the components, it was possible to distinguish two different constituents primarily from geopolymeric matrix (figures 49-51).

Figure 50 shows the presence of "rounded included", with a density much lower than the geopolymer; these bubbles, attributable to air remained incorporated during the mixing process are confirmed by microscopic observations; in addition by this technique it is possible to see their distribution within the sample volume.

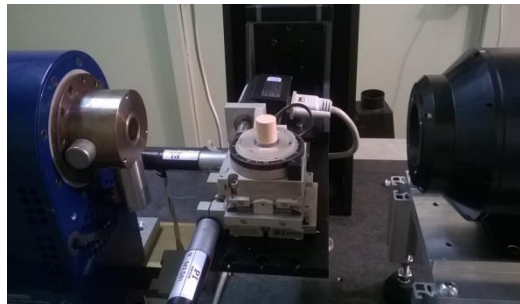
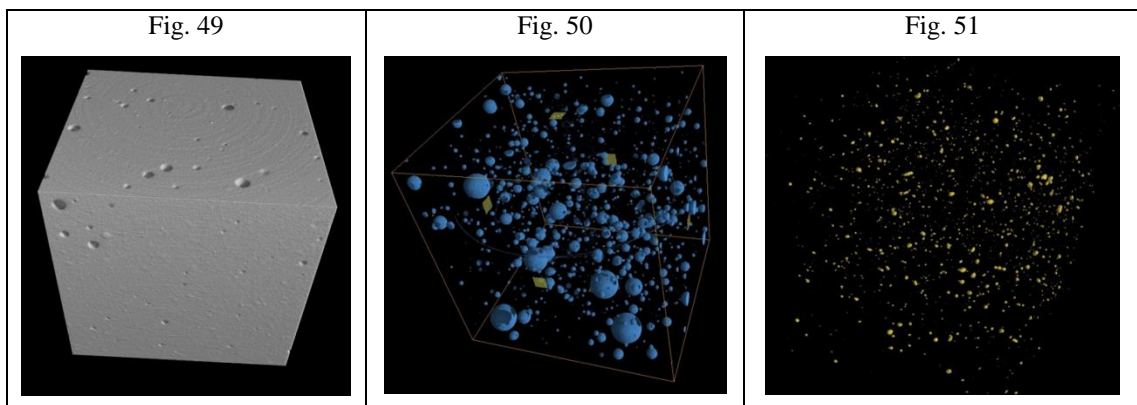


Figure 48. Micro CT Equipment

Figure 51 shows the presence of small included with an intermediate density between geopolymer and air. Currently the tests do not allow us to attribute a precise compound, but it could be assumed that they are small fractions of unreacted alkaline solution trapped in the porosity of the material.



Figures 54-56. 3D images of geopolymeric binders GEO-BS6-650

3.3.2.6 Mechanical properties

Finally, but not least, the results of mechanical tests have provided very interesting results on the ability of geopolymerization, such as right compactness/ powder cementation, but also on the correlation between a type of raw material (especially as a function on how it is treated) and the variation of the mechanical strength of the finished product.


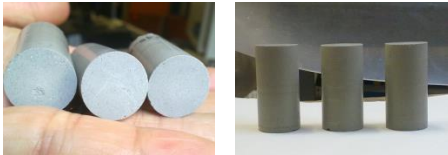
In addition to the mechanical strength, also the failure mode of the samples has provided important information on the microstructure.

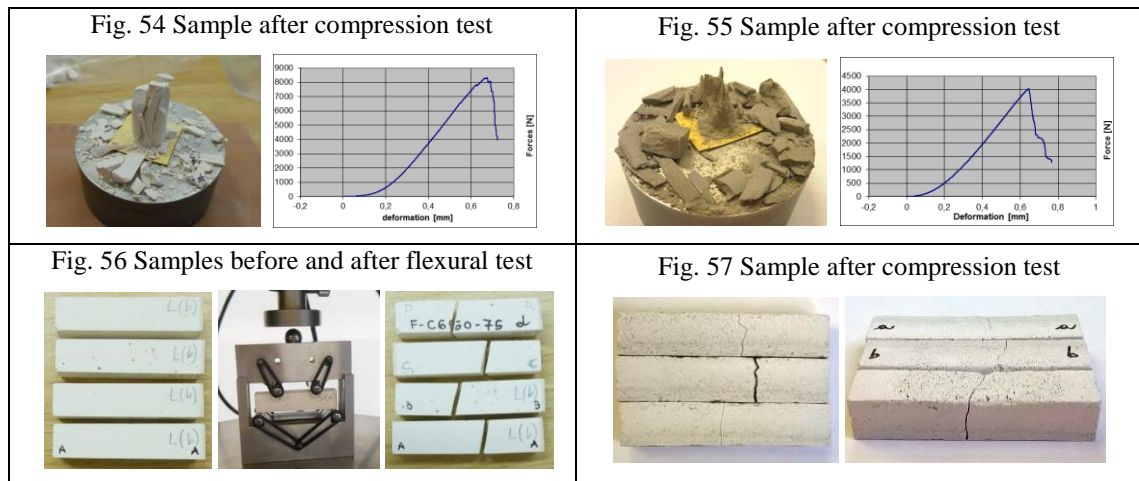
It has been seen that the geopolymers produced with thermal treated MKs are characterized by a higher compression resistance and bending strength compared to those with " mechano-chemical MKs " (table 7). The higher standard deviation, unfortunately affecting the results, indicates poor repeatability of the properties of the mixture. Values of compression resistance greater than 50 MPa, and the breaking mode indicate that the "thermal geopolymers" exhibit some of the characteristics of hard and brittle materials.

On the contrary, geopolymers "mechano-chemically-activated" show a lower resistance, but a more homogeneous behavior. Also the macroscopic aspect results very different: in this last case, the obtained material seems to be real cement.

Sample	% Al ₂ O ₃	Compression S (MPa) After 28 days	Flexural S (MPa) After 28 days
GEO-BS4-650	75	55.09 ± 6.26	9.65 ± 1.40
GEO-BS6-650	75	51.40 ± 10.00	7.58 ± 4.00
GEO-BS4-30'_90	90	36.92 ± 3.72	4.80 ± 0.59
GEO-BS4-30'_85	85	35.46 ± 1.75	5.43 ± 0.54



Table 7. Compression and flexural values of geopolimeric binders



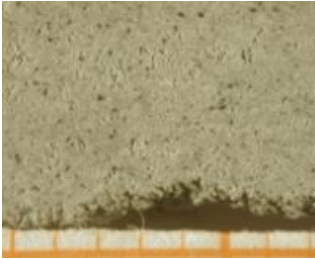
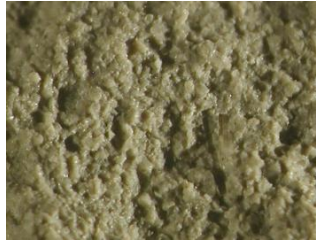
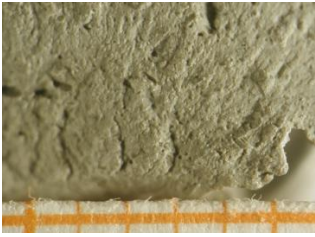

GEO-BS4-650	GEO-BS4-30'_85
<p>Fig. 52 Sample before compression test</p> 	<p>Fig. 53 Sample before compression test</p> 



3.3.2.7 Microscopic observation

The binders have been observed at stereoscopic microscope under reflected light. In Figures 58-65 micrographs showing different microstructures are reported.. GEO-BS4-30'_90/85 have a coarser microstructure with the presence of pores and microcrystals. The aspect is quite similar to that of very fine concrete or cement. On the contrary the matrices of GEO-BS4/BS6-650 binders is practically amorphous and well compacted; no crystals are visible. It seems a ceramic paste (like gres) with some well-defined pores. These different microstructures can be due to the morphology of the particles after the two different treatments. Thermal treatment causes the agglomeration of the particles, but this new agglomerates are characterized by high porosity so that when the grains are in contact with the alkaline solution they are quite completely involved in the reaction of geopolymerization. In the GEO-BS4-30'_90/85 binder, the aggregation of the grains subsequently to the grinding provokes only a high packaging, so that the grains maintain their morphology.

Sample	Microstructural aspect 12-20 X	Microstructural aspect 40-50 X
GEO-BS4-650	Fig. 58 	Fig. 59 

GEO-BS6-650	Fig. 60 	Fig. 61 
GEO-BS4-30'_90	Fig. 62 	Fig. 63 
GEO-BS4-30'_85	Fig. 64 	Fig. 65 

3.3.2.8 Physical aspects

Another important parameter is the porosity of these materials. As reported in table 8, geopolymeric binders are characterized by high porosity (30-40%). The pore-size distribution evidences a mode in the correspondence of 0.01 micron. The high porosity and the mode seem to mean that the geopolymerization reaction allows the formation of micro-pores linked to each other. This could represent a good transpiring property.

Sample	Density (g/cm ³)	Accessible Porosity (%)	Average pore diameter (μm)
GEO-BS4-650	1,60 ± 0,03	38.01	0.0126
GEO-BS6-650	1,50 ± 0.01	40.99	0.0115
GEO-BS4-30'_90	1,22 ± 0,02	35.61	0.0131
GEO-BS4-30'_85	1,28 ± 0,06	25.12	0.0132

Table 8. Physical aspects of binders

Fig. 66

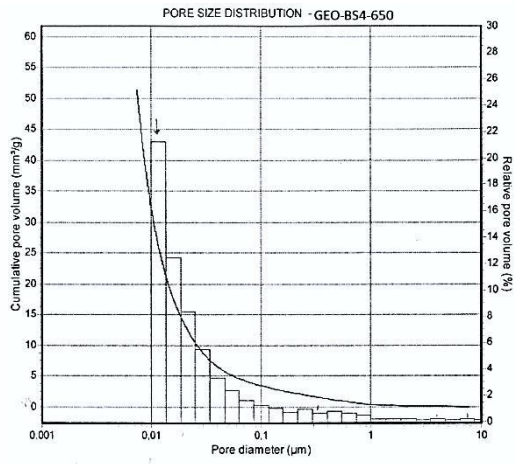


Fig. 67

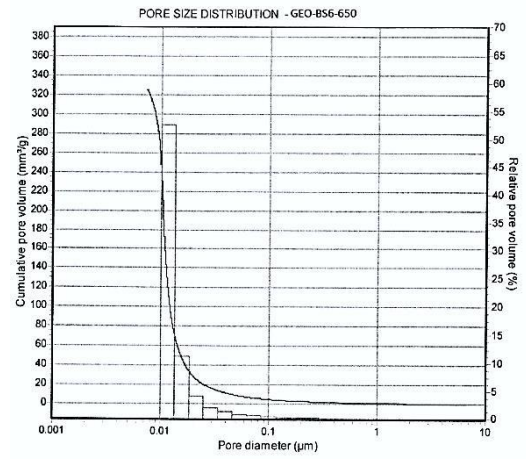


Fig. 68

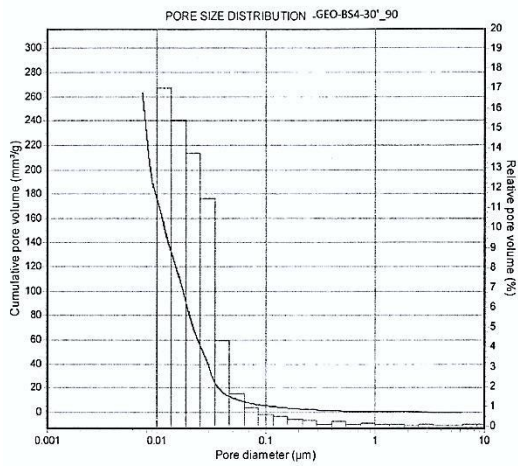
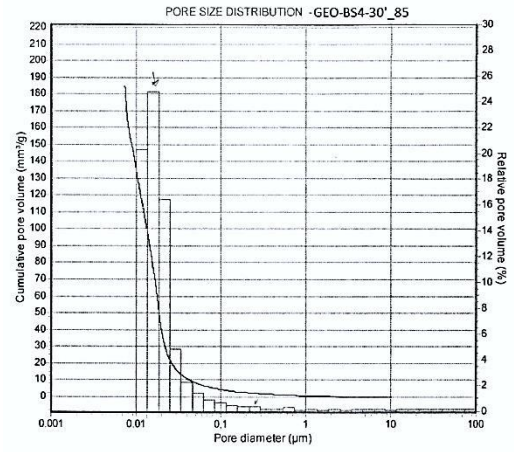


Fig. 69



Figures 66-69. Pore size distribution of binders

Chapter 4

Geopolymeric composites

4.1

Introduction

The characterization of binders in addition to being a study on the behavior and properties of these innovative materials, it was aimed at the realization of so-called composite mixtures (figure 1). In these materials various kinds of fillers or aggregates, with functionalizing function and or changing the final properties, were added to the binder, how is usually for all traditional materials (mortars, cements, clays, etc. ..).

These fillers can be of various nature: organic, inorganic, compact, porous, fibrous. They can be added in various amounts, up to the achievement of the desired properties.

When they are in the form of powders, they influence physical and mechanical properties such as by stabilizing the structure of the material, by limiting the shrinkage during drying, also avoiding fractures and fissures, in some cases..

The first step in the production and validation of an innovative material is to understand how the traditional fillers (for example, those which normally are used for the cement) can be react with it from chemically, physically and mechanically point of view.

In this study various tests, adding "solid" fillers such as sand, rock powders, lightweight aggregates, inorganic and organic fibers were conducted.

We have been also considered inorganic pigments, which are constituted by inert powders, more or less, and therefore only physically interacting with the geopolymeric matrix.

Liquid pigments has been also added, because they are commercially available in this state, such as organic dyes and chemical additives that allow to vary the workability of the mixtures. These are generally organic polymers (acrylic, methacrylic, PEG, etc ..).

This chapter is divided into three paragraphs in which the composite are described according to purposes: functionalized (sands, etc ...), colored (pigments and dyes) and different workability (with organic polymer additives).

The binders used were GEO-BS4-650 and GEO-BS4-30'_85 based on MK-BS4 and GEO-BS6-650 based on MK-BS6.

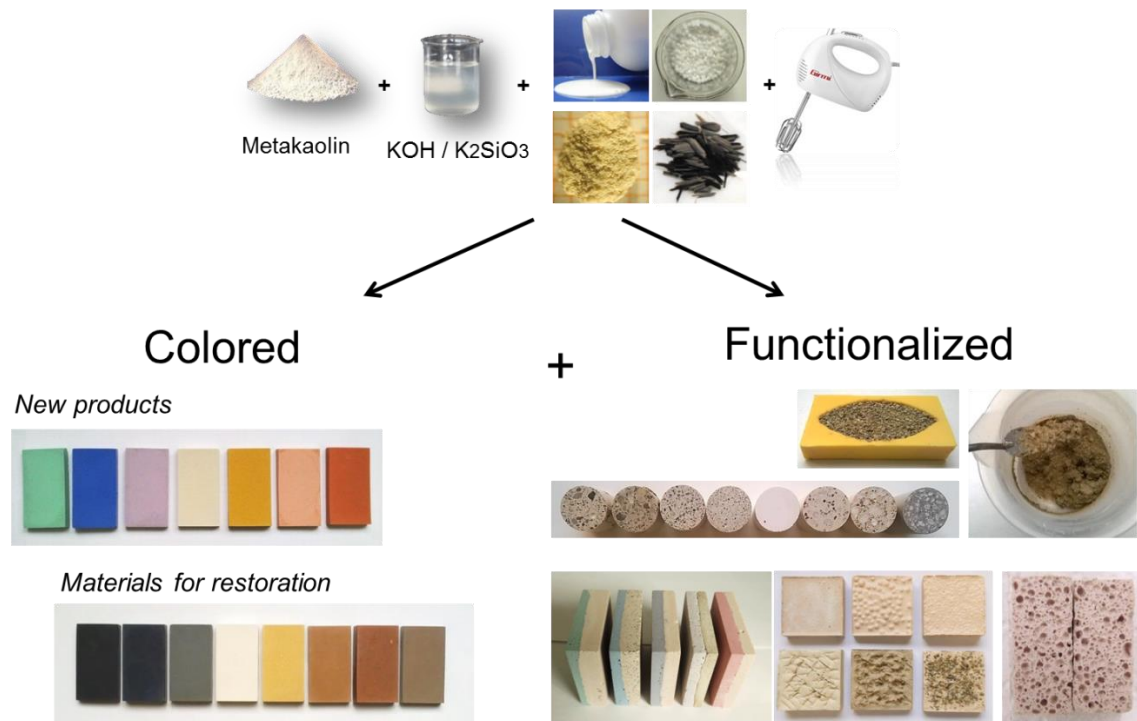


Figure 1. Schematic representation of composites production

4.2

Functionalized composites

The purpose of these composites was to obtain, whenever possible, interesting material effects from an aesthetic point of view in order to be used for applications in building or in restoration field.

4.2.1 Materials and methods

GEO-BS4-650 and GEO-BS4-30'_85 based on MK-BS4 and GEO-BS6-650 based on MK-BS6 were used to produce geopolymeric composites. The preparation procedure is very similar to the binders one and it is briefly reported below.

The abbreviations MK-T-BS4 and MK-T-BS6 indicate materials treated by thermal activation process (650°C for 2h), while MK-M-30'_BS4 by mechano-chemical process (grinding time = 30') and they were used to prepare geopolymeric functionalized composites for this PhD study.

Alkaline solutions were prepared by dissolving KOH pellets (85%, Sigma-Aldrich, Germany) into Potassium silicate solutions (Ingessil S.r.l, Italy) in order to achieve the following molar ratios : $\text{SiO}_2/\text{Al}_2\text{O}_3 = 3.6$; $\text{M}_2\text{O}/\text{Al}_2\text{O}_3 = 1$; $\text{H}_2\text{O}:\text{K}_2\text{O} = 10-20$.

The formulation step was described in Chap. 2.

Also in this case $\text{H}_2\text{O}/\text{K}_2\text{O}$ ratios were defined “a posteriori” on the basis of the different workability of the mixtures, but in general was in the range of 10-20.

The “aggregates” were selected by considering their chemical composition in order to limit their reactivity with alkaline solution.

The solid aggregates used for these formulations are reported below :

- with compact structure: natural sands, natural rock powders, (marble, gneiss, limestone and calcite).
- with porous structures: perlite, poraver, treated and untreated polystyrene grains (PS-T) (PS-V), respectively basalt fibers.

In table 1 are shown the properties of some of the aggregates reported above.

Type	Basalt fibers	Perlite grains	Pomice grains
Distributor	BASALTEX NV, Wevelgem – Belgio.	PERLITE ITALIANA Srl, Milano	PUMEX s.p.a. Lipari
Size	Diameter 10-19 mm, length 6mm	2-4 mm	0,85-3 mm
SiO ₂	49.58	74 -78	71,75
Al ₂ O ₃	14.48	11-14	12,33
K ₂ O	1.89	2- 4	-
Na ₂ O	2.10	3 -6	3,59
Fe ₂ O ₃	4.42	0,5 -1,5	1,98
FeO	-	-	0,02
CaO	8.50	1-2	0,70
MgO	5.10	0 - 0,5	0,12
MnO	0.17	-	0,07
TiO ₂	2.08	-	0,11

Table 1. Chemical composition of some aggregates

Type	Sand (Natura)	Marble powder	Trani Limestone powder	Gneiss powder	Maastricht stone grains
Distributor	Opificio Bio Aedilitia, Bondeno, Italy	-	-	-	-
Grain size	0- 2 mm	< 1 mm	< 1mm	< 1mm	0.6 – 4 mm
Chemical Composition	Silicon carbonate	Calcium carbonate	Calcium carbonate	silicate	Calcium carbonate

Table 2. Chemical and physical aspects of rock powders

4.2.2 Synthesis of geopolymers

A calculated quantity of potassium silicate solution was put into a becker, then a calculated amount of potassium hydroxide pellets was added.

The becker was put into a container with cold water in order to facilitate the cooling of the mixture and successively a weighted quantity of the metakaolin powder and the selected aggregates powders has been added and mixed by using a mechanical mixer for 5-15 minutes.

If necessary, a weighted quantity of distilled water was added in order to obtain a mixture suitable to be poured. The obtained mixture was poured into plastic or silicone molds (depending on the required shape); generally several samples for each mixture were prepared in order to obtained sufficient samples for the different tests.

Then the samples were sealed with *Parafilm* and subjected to the curing phase (the same of the binders): room temperature for 24h and then in oven at 60°C for 24h. After this time, the samples were removed from the molds and preserved into sealed envelopes for permitting an homogeneous and gradual drying.

After the “curing time” (generally 28 days at room temperature) the samples were analyzed as reported above.

Composites formulations are detailed described in table 2. Aggregates quantities (range 1-80% in Weight, calculated on the base of dehydrate geopolymeric binders) vary based on the intrinsic characteristic of each one, depending on grain size, porosity and expected results.

Preparation of the geopolymeric composites

In this chapter the composites are divided as follows:

- by using GEO-BS4-650 and GEO-BS4-30’_85 (part 1) in order to compare the “bonding performance” of geopolymeric binders derived from the same BS4;
- by using GEO-BS6-650 (part 2), in which different nature aggregates were used, even in admixture among themselves and with the addition for some of the organic additives.

Part 1- GEO-BS4-650 and GEO-BS4-30’_85 binders were prepared with:

- 1 - silicate and carbonate (calcite and dolomite containing) sand with grain dimensions comprised in the range 0.60-1.25 mm;
- 2 – basaltic choppers with the fibers 6 mm in length and 0.8 mm in diameter;
- 3 – perlite grains with dimension of grains less than 2 mm.

The perlite and the silicate sand were added in amount of 20% in weight, while the basaltic choppers in amount of 2% in weight.

Sample	Total Aggregate (%)	Type and percentage of each aggregate
GEO-BS4-650 + Per	20	20 % perlite 2-6 mm
GEO-BS4-650 + S	20	20 % sand 0.6-1,25mm
GEO-BS4-650 + BS	2	2% basalt fibers
GEO-BS4-30’_85 + Per	20	20 % perlite 2-6 mm
GEO-BS4-30’_85 + S	20	20 % sand 0.6-1,25mm
GEO-BS4-30’_85 + BS	2	2 % basalt fibers

Table 3. Composites formulations with MK-BS4

Part 2- GEO-BS6-650 binder was prepared with sand, rock powders, perlite, PS-T/V, calcium carbonate, added in different amount from 6.5 to 82% in weight.

In table 4 are reported all the produced formulation also those with organic additives and in figures 2 (a-f) are shown some steps of preparation process.

Sample	Total Aggregate (%)	Type and percentage of each aggregate
GEO 1	60	20 % sand 0-0.60 mm 20 % sand 0.60-1.25 mm 20 % sand 1.25-3.00 mm
GEO 1A	61	20 % sand 0-0.60 mm 20 % sand 0.60-1.25 mm 20 % sand 1.25-3.00 mm 1% Flux
GEO 2	80	26.6 % sand 0-0.60 mm 26.6 % sand 0.60-1.25 mm 26.6 % sand 1.25-3.00 mm
GEO 2A	80	80% marble powder 1 mm
GEO 3	80	26.6 % CaCO ₃ microniz. 26.6 % sand 0-0.60 mm 26.6 % sand 0.60-1.25 mm
GEO 4	80	40 % CaCO ₃ microniz. 40 % sand 0-0.60 mm
GEO 4A	81	40 % CaCO ₃ microniz. 40 % sand 0-0.60 mm 1% Flux
GEO 4B	82	40 % CaCO ₃ microniz. 40 % sand 0-0.60 mm 1% Flux 1% CaO
GEO 4C	80	40 % CaCO ₃ microniz. 40 % sand 0-0.60 mm 1% Flux 0.5 % CaO
GEO 5	80	80 % CaCO ₃ microniz
GEO 6	50	20 % sand 0-0.60 mm 20 % sand 0.60-1.25 mm 10 % perlite 2.00-4.00 mm
GEO 6A	60	24 % sand 0-0.60 mm 24 % sand 0.60-1.25 mm 12 % perlite 2.00-4.00 mm

GEO 6B	52	20 % CaCO ₃ microniz. 20 % sand 0-0.60 mm 12 % perlite 2.00-4.00 mm
GEO 6D	52,5	40 % sand 0-0.60 mm 12.5 % perlite 2.00-4.00 mm
GEO 6E	52,5	20 % CaCO ₃ microniz. 20 % sand 0-0.60 mm 12.5 % perlite 2.00-4.00 mm
GEO 7	50	25 % sand 0.60-1.25 mm 25 % perlite 2.00-4.00 mm
GEO 7A	60	35 % sand 0.60-1.25 mm 25 % perlite 2.00-4.00 mm
GEO 8	20	20 % perlite 0.5-3.5 mm
GEO 8A	40	40 % perlite 0.5-3.5 mm
GEO 9	30	15 % perlite 0.5-3.5 mm 15 % slate
GEO 9A	30	20 % perlite 0.5-3.5 mm 10 % slate
GEO 10	25.5	10 % perlite 0.5-3.5 mm 15 % slate 0.5 % pearls PS-T 2 mm
GEO 10 A	25.5	10 % perlite 0.5-3.5 mm 15 % slate 0.5 % pearls PS-T 2 mm (+ metal net)
GEO 11	10.5	10 % perlite 0.5-3.5 mm 0.5 % pearls PS-V 2/3-6 mm
GEO 11A	10.5	10 % perlite 0.5-3.5 mm 0.5 % pearls PS-T 2/3-6 mm
GEO 12	9	8 % perlite 0.5-3.5 mm 1 % pearls PS-V 2/3-6 mm
GEO 12A	9	8 % perlite 0.5-3.5 mm 1 % pearls PS-T 2/3-6 mm
GEO 13	6.5	5 % perlite 0.5-3.5 mm 1.5 % pearls PS-T 2/3-6 mm

GEO 13A	6.5	5 % perlite 0.5-3.5 mm 1.5 % pearls PS-T 2/3-6 mm
GEO 14	60	60 % gneiss powder < 1 mm
GEO 15	60	60 % Apuan marble powder < 1 mm
GEO 16	60	60 % Trani's limestone powder < 1 mm
GEO 17	60	60 % Verona's limestone powder < 1 mm

Table 4. Composites formulations with MK-BS6



Figures 2 (a-f) . Composite preparation

4.2.3 Funzionalized composites characterization

Geopolymeric composites were characterized with some of the analytical techniques used for the geopolymeric binders. For these formulations particular attention was devoted to physical, microstructural and mechanical properties.

Microscopic observations, SEM observations and Micro CT were used to determine the morphological features, porosity and flaws. Mechanical tests (uniaxial compression and flexural strength) were used to assess the mechanical resistance of the materials.

4.2.4 Result and discussion

4.2.4.1 Microscopic observations

From microscopic observations it was possible to observe that some aggregates are perfectly incorporated in the geopolymeric matrix, while basalt fibers are detached. The composites made of sand show micro fractures, which may depend from their rigid nature, inside geopolymeric matrix. In fact, this type of defect is much less evident in geopolymeric composites made of perlite, which seems to perfectly interact with the binder (figures in table 5 and 6). This behavior is better visible in the binder, characterized by hardness and brittleness properties.

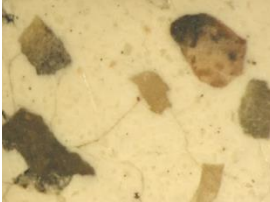
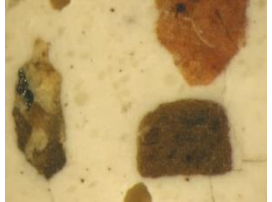










GEO-BS4-650 + sand	 40 X	 64 X
GEO-BS4-650 + perlite	 20 X	 40 X
GEO-BS4-650 + basalt fibers	 20 X	 40 X
GEO-BS4-30'_85 + sand	 20 X	 40 X
GEO-BS4-30'_85 + perlite	 40X	 40 X
GEO-BS4-30'_85 + basalt fibers	 40 X	 64 X

Table 5. Microscopic observation of composites GEO-BS4-650 and GEO-BS4-30'_85

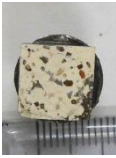
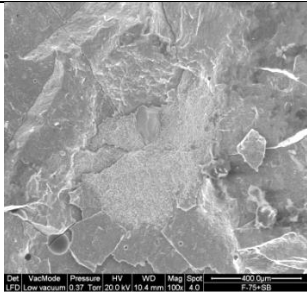
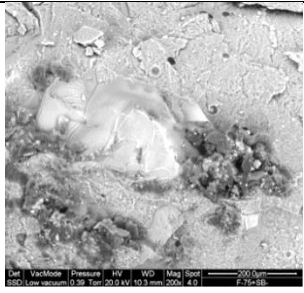

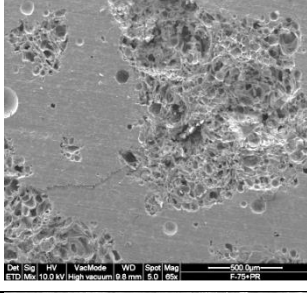
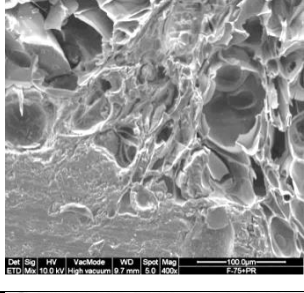
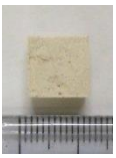

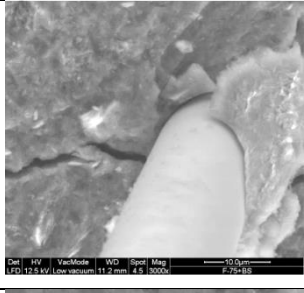
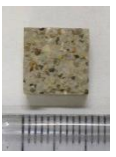
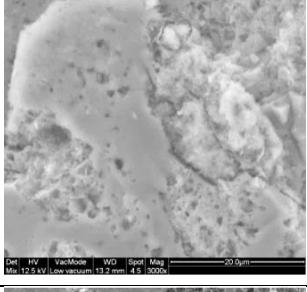
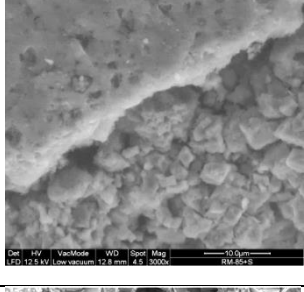

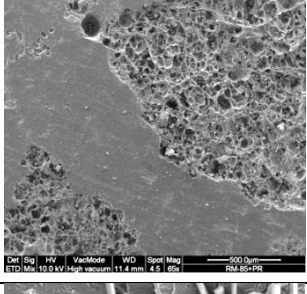
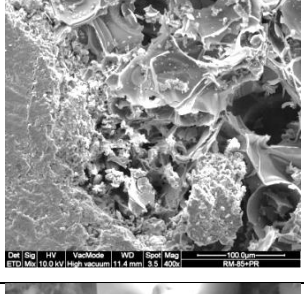

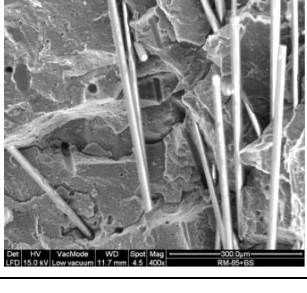
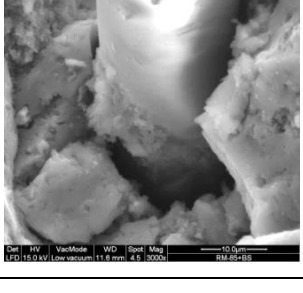
GEO-BS4-650 + sand 	 100 X	 200 X
GEO-BS4-650 + perlite 	 65 X	 400 X
GEO-BS4-650 + basalt fibers 	 200 X	 3000 X
GEO-BS4-30' _85 + sand 	 3000 X	 3000 X
GEO-BS4-30' _85 + perlite 	 65 X	 400 X
GEO-BS4-30' _85 + basalt fibers 	 400 X	 3000 X

Table 6. SEM observation of composites GEO-BS4-650 and GEO-BS4-30' _85

4.2.4.2 Micro CT

The geopolymeric composites GEO-BS6-650 with perlite and sand were analyzed in order to verify the homogeneous distribution of the aggregates inside the bulk.

The figure 3 shows how sand and perlite are well distributed in the entire volume of binders. Another important aspect is the presence of many air bubbles, probably trapped during mixing in the composites obtained by using sand .

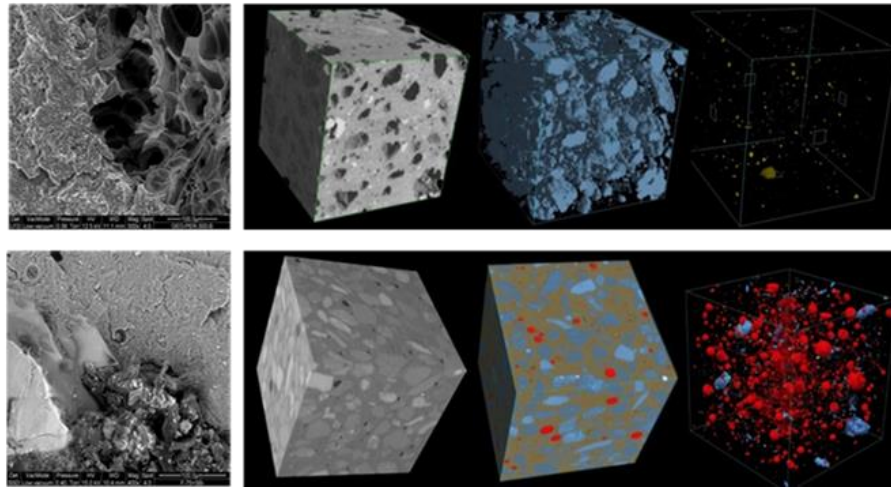


Figure 3 SEM images of sample with perlite (top) and sand (bottom) compared with 3D reconstructions by Micro Ct analysis.

4.2.4.3 Mechanical properties

The mechanical strength tests were carried out following the same parameters used for the binders..

By comparing the data of the various formulations obtained by compression and bending tests can be noted as the addition of aggregate causes on average a lowering of resistance values (table 7).

The only exception is the formulation GEO-BS4-30'_85 with basalt fibers, in which the compressive strength value is only slightly higher than the binder.

In general, for all the geopolymeric composites, despite the resistance decreases, there is a greater homogeneity of the results, as can be seen by observing the standard deviations associated with the average values reported. The assumptions related to these phenomena are different and yet to be investigated.

To obtain more information with respect to the morphology of the materials analyses in light and electron microscopy were performed. In tables 7 and 8 the results are reported.

Sample	Compression S (MPa)	Flexural S (MPa)	Density (g/cm ³)
F-75 + PER	22.87 ± 1.67	4.39 ± 0.39	1.21 ± 0.03
F-75 + S	30.40 ± 6.30	4.60 ± 0.21	1.72 ± 0.02
F-75 + BS	23.90 ± 3.80	5.96 ± 1.10	1.50 ± 0.02
RM-85 + PER	7.53 ± 0.39	2.34 ± 0.14	0.96 ± 0.02
RM-85 + S	21.73 ± 1.06	5.36 ± 1.54	1.58 ± 0.11
RM-85 + BS	33.80 ± 1.50	2.91 ± 0.45	1.46 ± 0.02

Table 7. Results of mechanical test of composites GEO-BS4-650 and GEO-BS4-30'_85

GEO-BS4-650 + sand	
GEO-BS4-650 + perlite	
GEO-BS4-650 + basalt fibers	
GEO-BS4-30'_85 + sand	
GEO-BS4-30'_85 + perlite	
GEO-BS4-30'_85 + basalt fibers	

Table 8. Images of GEO-BS4-650 and GEO-BS4-30'_85 composites after mechanical test

In tables 9 and 10, the mechanical strength values of the composites with GEO-BS6-650 and some images are reported.

Sample	Compression S (MPa)	Flexural S(MPa)
GEO 1	31.4 ± 6.7	7.66 ± 0.31
GEO 1A	-	-
GEO 2	23.5 ± 2.4	4.62 ± 0.44
GEO 2A	29.1 ± 5.2	7.50 ± 0.56
GEO 3	13.67 ± 1.27	3.49 ± 0.40
GEO 4	12.46 ± 0.61	4.42 ± 1.00
GEO 4A	24.3 ± 2.0	5.93 ± 0.17
GEO 4B	25.1 ± 0.5	6.22 ± 0.72
GEO 4C	28.0 ± 1.0	6.82 ± 0.35
GEO 5	4.36 ± 0.74	2.01 ± 0.34
GEO 6	12.21 ± 0.72	3.90 ± 1.08
GEO 6A	45.4 ± 11.3	9.22 ± 0.16
GEO 6B	30.6 ± 2.7	6.35 ± 0.30
GEO 6D	12.2 ± 5.8	1.94 ± 2.13
GEO 6E	15.5 ± 2.9	4.39 ± 0.23
GEO 7	16.17 ± 3.19	3.89 ± 0.53
GEO 7A	17.6 ± 1.2	4.81 ± 1.18
GEO 8	25.73 ± 5.21	5.53 ± 0.52
GEO 8A	23.48 ± 3.76	5.28 ± 0.54
GEO 9	24.16 ± 3.61	4.24 ± 0.46
GEO 10	2.51 ± 0.05	0.97 ± 0.13
GEO 10 A	-	1.88 ± 0.27
GEO 11	6.57 ± 0.69	2.37 ± 0.11
GEO 11A	9.84 ± 1.40	2.67 ± 0.21
GEO 12	6.03 ± 0.88	2.71 ± 0.12
GEO 12A	6.82 ± 0.96	3.20 ± 0.17
GEO 13	4.28 ± 0.35	1.75 ± 0.15
GEO 13A	3.76 ± 0.12	1.78 ± 0.21
GEO 14	59.25 ± 9.17	12.2 ± 0.79
GEO 15	54.77 ± 6.69	9.70 ± 0.81

GEO 16	39.11 ± 6.45	8.27 ± 0.89
GEO 17	47.94 ± 0.76	8.79 ± 0.61

Table 9. Mechanical strength values of the samples produced with GEO-BS6-650



Table 10. Composites with GEO-BS6-650 after mechanical tests

The data obtained show a very broad range of resistance values depending on the types and quantities of aggregate. In general, hard and compact ones allow to obtain higher strength. Increasing the percentage of the aggregate the resistance tends to decline but at the same time the values are in a very small range, so more homogeneous.

Lightweight and porous aggregates, especially of organic nature (PS), drastically diminish the performance of the mixtures, coming to compression values lower than 10 MPa.

Very interesting are the results of the composites obtained by adding the two different components (compact and porous): gradually changing the percentages of the two components the strength can be modulated.

4.3

Colored composites

These composites are designed to evaluate two main aspects:

- the ability of geopolymeric binder to be mixed with powders of micrometric dimensions (similar to those of the MK) by evaluating in particular the mechanical behavior,
- the binder ability to be colored in a stable and homogeneous way through both inorganic and organic dyes.

The two types were chosen in order to obtain a wider color range: the most stable inorganic pigments generally based on silicate (e.g. Ultramarine blue / synthetic Lapis lazuli) or ferrous elements (e.g. natural hearts) limits the chromatic possibilities.

In contrast, the organic dyes are characterized by a higher chromatic vastness.

4.3.1 Materials and methods

In the production of colored geopolymers only the GEO-BS6-650 binder was used.

Geopolymeric formulations were prepared as described in 4.2.1 and also in this case H_2O/K_2O ratios were chosen “a posteriori” depending the workability of the mixture.

Inorganic pigments and organic dyes were selected on the bases of their chemical stability in order to limit their reactivity with alkaline solution.

All the colored inorganic pigments and acrylic dyes were purchased in specialized art stores.

4.3.2 Synthesis of geopolymer

Synthesis was performed as described for functionalized composites.

The quantities of the colored filler for each formulation is about 5% in weight, calculated on the base of dehydrate geopolymeric binders.

In order to compare the stability of the dyes and some characteristics including the mechanical resistances, six formulations with organic pigments and organic dyes were prepared following the procedure described above.

The pigment powders were added to the MK and homogenized, prior to mixing with the alkaline solution, on the contrary, the organic dyes were added after 1 minute from the start of mixing or in any case when the binder was already at an homogeneous and fluid condition (figures in table 11).

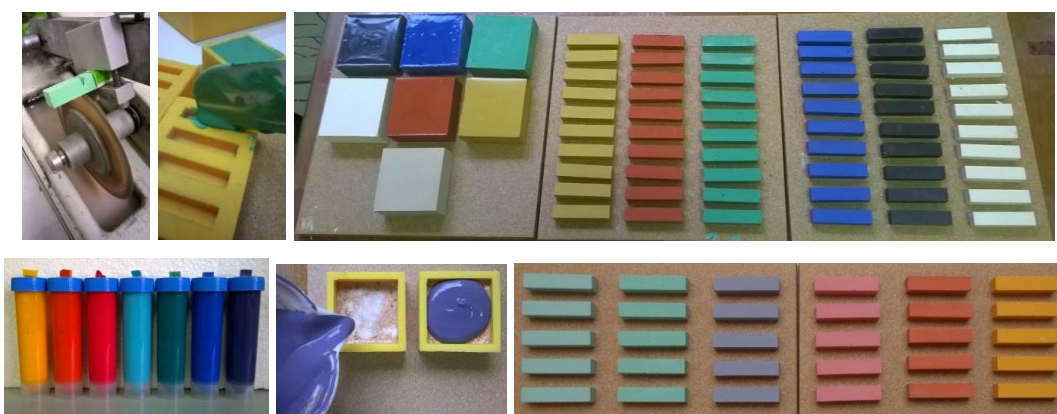


Table 11. preparation of geopolymeric composites

4.3.3 Colored composites characterization

Colored composites were characterized by XRF for the chemical composition of inorganic pigments, SEM observations, Mercury Intrusion Porosimetry (MPI) and Mechanical tests (uniaxial compression and flexural strength) were used to assess the mechanical resistance of the materials.

4.3.4 Result and discussion

4.3.4.1 XRF

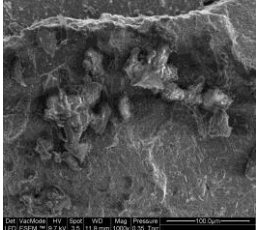
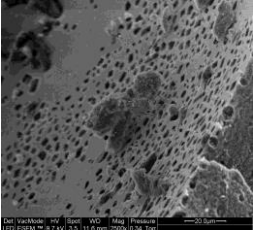
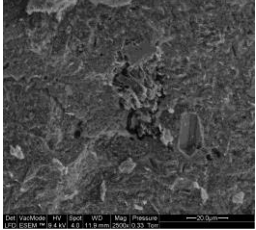
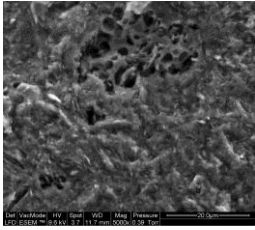
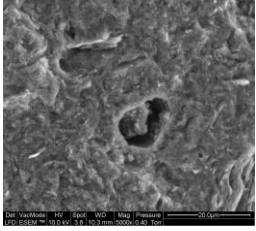
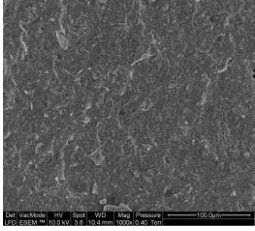
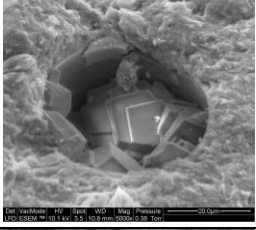
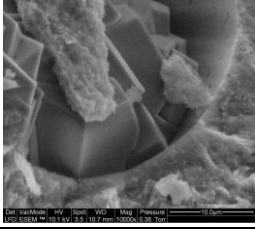
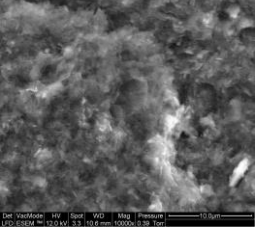
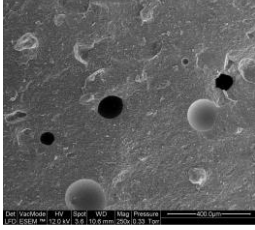
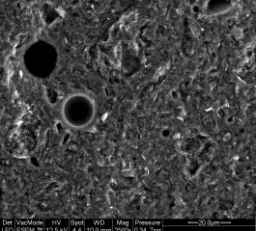
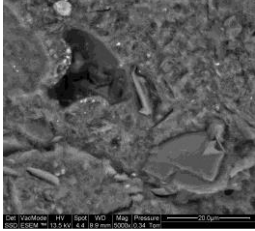
The chemical characterization of some inorganic pigments was performed using XRF technique. Is possible to note that all these pigments have a chemical composition very stable in alkaline conditions: they are made of Ca, Fe, Si and Ti. White and Black pigments are not reported in the table, but white is completely constitute by TiO_2 , while black is a “vine black” consisting in carbon, insoluble carbon compounds and ashes.

Oxide %	Yellow	Orange	Red	Green 1	Green 2	Blue
CaO	17,38	98,99	78,73	83,47	76,37	8,98
Fe ₂ O ₃	52,74	-	20,18	-	14,22	0,89
TiO ₂	0,28	-	-	11,91	3,80	0,05
SiO ₂	3,65	0,21	0,33	0,19	1,89	26,00
NiO	-	-	-	0,77	1,24	0,10
MgO	1,21	0,28	0,39	0,25	0,87	0,40
Al ₂ O ₃	1,82	0,15	0,16	0,19	0,49	16,78
SO ₃	22,15	0,19	0,17	0,34	0,44	21,45
CuO	-	-	-	0,17	0,28	-
P ₂ O ₅	0,08	0,04	0,01	0,03	0,12	11,03
Cl	-	-	-	1,16	0,12	0,18
K ₂ O	0,52	-	-	-	0,12	0,74
SrO	0,16	0,04	0,02	0,05	0,03	0,03
Na ₂ O	-	0,10	-	0,26	-	12,85
MnO	-	-	-	-	-	0,52
Sb ₂ O ₃	-	-	-	1,22	-	-

Table 12. Chemical composition of the some pigments used

4.3.4.2 SEM observation

The SEM images show that bubbles and defects into the geopolymeric matrix. Each pigment seems to be characterized by a different overall structure and probably a sort of interaction between the two components takes place.

GEO WHITE-I	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm
GEO YELLOW-I	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm
GEO RED-I	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm
GEO GREEN(1)-I	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm
GEO BLUE-I	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm
GEO BLACK	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm	 Det: VacMode HV: 20.0kV Spot: 1.0 Magn: 1000x WD: 10.0mm LTO: 0.00mm

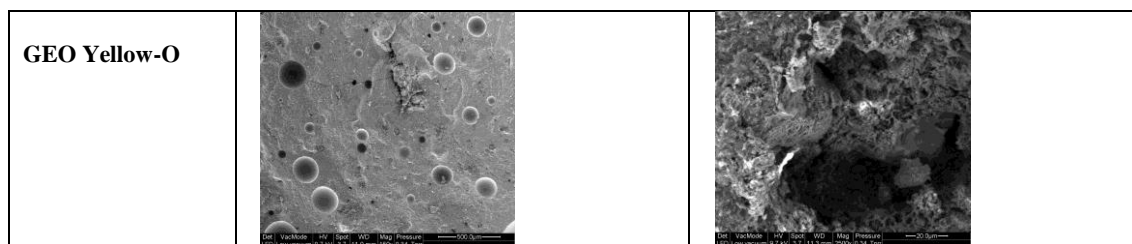


Table 13. SEM images of colored composites

4.3.4.3 Mechanical tests

Despite the presence of defects, the mechanical tests give very interesting results, comparable and in some cases even higher those obtained for the binders (table 14).

SAMPLE	Compression S (MPa)	Flexural S (MPa)
GEO WHITE-I	65.23 ± 8.92	8.69 ± 1.00
GEO YELLOW-I	60.25 ± 19.19	5.81 ± 1.09
GEO RED-I	62.42 ± 12.33	7.35 ± 0.36
GEO GREEN(1)-I	53.96 ± 13.58	6.72 ± 0.61
GEO BLUE-I	65.01 ± 18.78	7.28 ± 0.93
GEO BLACK	46.91 ± 4.02	5.62 ± 0.89
GEO Yellow-O	53.0 ± 5.8	6.85 ± 0.95
GEO Pink-O	68.5 ± 10.4	7.36 ± 0.63
GEO Red-O	46.5 ± 6.9	4.32 ± 3.10
GEO Green-O	61.0 ± 4.3	6.43 ± 1.44
GEO Blue-O	64.3 ± 3.7	7.20 ± 0.47
GEO Violet-O	60.6 ± 10.0	7.78 ± 0.35

Table 14. Mechanical resistance of colored composites
(I = with inorganic pigments; O = with organic dyes)

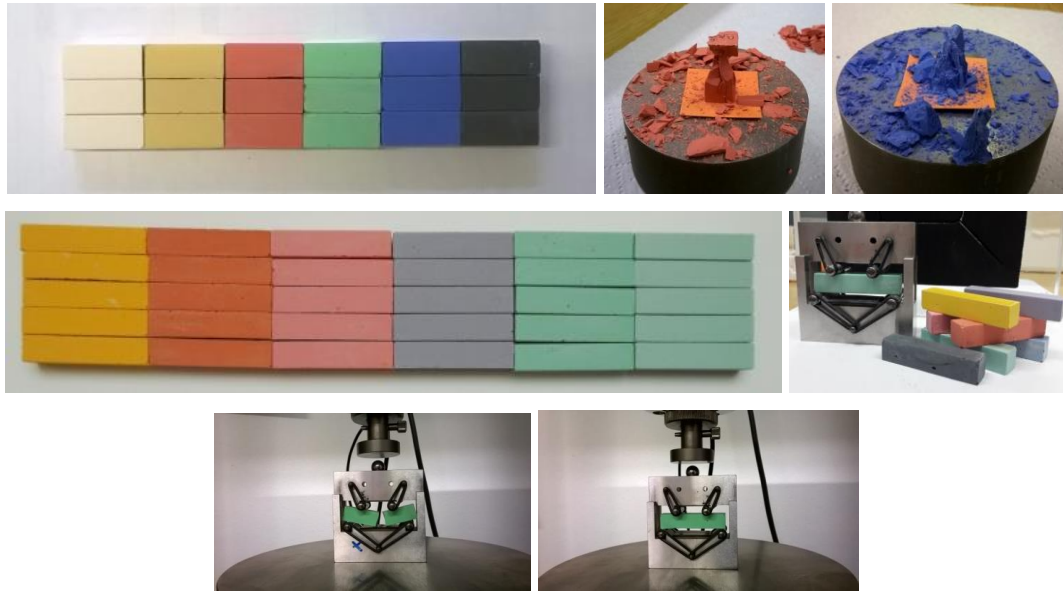
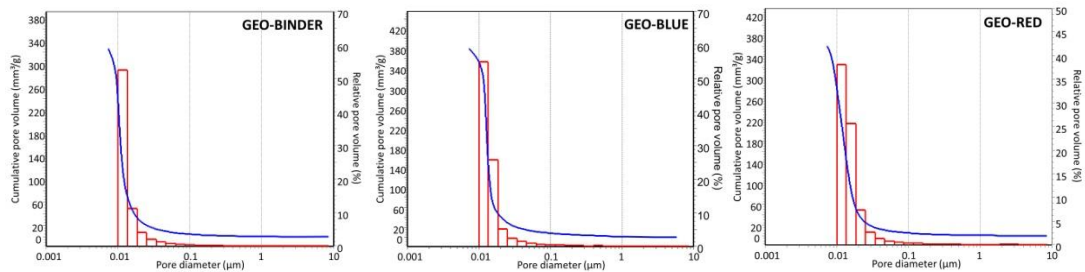


Table 15. Images of colored composites before and after mechanical tests

4.3.4.4 Porosimetric analysis

It is possible to note that the colored geopolymers exhibit a total open porosity value around 40% and a pore size distribution very similar to the binders alone (figures 4 a-c).



Figures 4 a-c. Pore diameter distribution of binders and red and blue composite

The agreeable aesthetic aspect in conjunction with characteristics of compactness have allowed us to test these materials for the restoration and the production of artistic objects, for example as mosaic tiles. Tablets of colored geopolymers with a thickness of approximately 10 mm were produced (figure 5). These were cut in order to obtain suitable pieces with variable dimensions and used as tiles in modern artifacts or inserted into ancient artworks into both traditional mortars and geopolymeric mixtures.



Figures 5. Colored tablets for mosaic tesserae

4.4

Chemically Additived Composites

The aim of this test was to evaluate whether some commercial additives, used for the production of lime-based mortars and cements, were also compatible with geopolymeric materials. Some of these additives have the purpose of increasing the wettability of the material, prolong or shorten the workability (the socket retardants or precursors), others as "simple" thinners.

Since the theme is very complex, as it enters the field of "hybrid" materials in which inorganic and organic polymers are mixed and coexist, many more experimentation is necessary in order to better understand the reaction mechanisms of these highly complex systems. Here some preliminary results are reported.

4.4.1 Materials and methods

In the production of colored only the GEO-BS4-650 binder was used.

Geopolymeric formulations were prepared as described in 4.2.1

Inorganic pigments and organic dyes were selected on the bases of their chemical stability in order to limit their reactivity with alkaline solution.

Commercial organic polymer additives (PEG, PAA, acrylic resins) were provided by specialized Companies.

4.4.2 Geopolymer's synthesis

Synthesis was performed as described for functionalized composites and the additives were introduced in different quantities of 1, 5 and 10 % in weight and their characteristics are reported in table 16.

Commercial name	Physical state	Distributor
FLUX	powder	Vinavil
VINAVIL 5603 P	powder	Vinavil
CELLULOSE	powder	Sigma Aldrich
STARCH	powder	Sigma Aldrich
SODIUM GLUCONATE	liquid	Sigma Aldrich
METHIL CELLULOSE	liquid	Vinavil
ACRYLIC 33	liquid	Bresciani

ISOLASTIC	liquid	Mapei
CRILAT A 117	liquid	Vinavil
CRILAT A 815	liquid	Vinavil
PEG 400	liquid	Sigma Aldrich

Table 16. Commercial additives

4.4.3 Mechanical characterization

They were characterized by uniaxial compression and flexural strength tests to assess the mechanical resistance of the materials. The results are reported in table 17.

SAMPLE	% Additive	Compression S (MPa)	Flexural S (MPa)
GEO FLUX	1	50.97 ± 6.87	8.84 ± 1.25
GEO 5603	1	78.31 ± 23.72	9.90 ± 0.79
GEO CELL	5	88.63 ± 5.48	8.98 ± 0.47
GEO AMI	5	64.34 ± 6.56	8.32 ± 1.09
GEO GLU	1	77.30 ± 16.37	7.70 ± 1.65
GEO MC	1	48.10 ± 15.97	5.01 ± 0.20
GEO AC33	1	76.72 ± 21.95	7.36 ± 0.60
GEO ISOL	1	83.52 ± 12.02	7.75 ± 1.11
GEO 117	1	76.64 ± 35.76	8.10 ± 0.39
GEO 815	1	61.70 ± 10.93	8.48 ± 0.71
GEO PEG 400-1	1	80.71 ± 22.18	10.96 ± 0.52
GEO PEG 400-10	10	50.24 ± 8.71	7.77 ± 1.37

Table 17. Mechanical resistance of composites

The use of these additives varies the workability of some geopolymeric formulations; in particular they make plastic and thixotropic a material that was initially different.

Despite the values of the mechanical tests highlight that in general any additive can improve the performance of the material (at least in compressive strength), the workability behaviors are quite different. Almost all make the geopolymer more fluid, also increasing the setting time. Only two conferred thixotropic behavior to the mixture allowing to apply it into the molds with “spatula”. This aspect is particularly important from the point of view of the material handling capacity.

This feature has allowed us to also test the ability to extrude the material thanks to "pastry bag" and syringes.

The results of this experiment are shown in the figures of table 18.

The following composites are the sum of the whole experience made. The mixtures of geopolimerich mortars and cupcakes are made with all three types discussed by the adding of sandy aggregate, colorant and additive agents.



Table 18. Colored and additives composites

4.5 Prototypes

Some complex prototypes developed in this study are in the figures below. In addition to the particular innovative materials attention it has been given to the processing technology and application of the individual first and then mixtures of different blends in contact to each other.

Direct application



Prototypes

Pre-casting mould



Colored geopolymers: mosaic tesserae or jewels



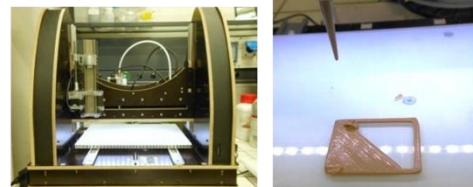
15 x 15 cm

Additive geopolymers: 3D printing



Preliminary viscosity tests for 3D printing

Prototypes



IN PROGRESS.....

Chapter 5

Applications

In this chapter are schematically summarized some examples of conservative restorations in which some geopolymeric composites have been applied. These case studies have allowed to test, on real cases, the ability of materials to carry out certain functions, both functional and aesthetic.

Apart from the colored tesserae (5.2) the attention was also devoted to movable support for replacing detached mosaic or wall painting fragments.

For this purpose, lightweight panels were designed. They were obtained by adding different percentages of lightweight aggregates, in particular perlite, to the binder.

Two different ways are chosen: pre-casted panels (5.1) or direct application (5.2) that means pouring the geopolymeric mixture on the retro side of restoration mortars.

Some images that summarize the interventions are reported below. In Tables 1 and 2 are inserted some data such as mechanical strength and microscopic observations of the 6 formulations used in these various studies.

5.1

Conservative intervention of “Madonna delle Grazie” a painting on slate slab

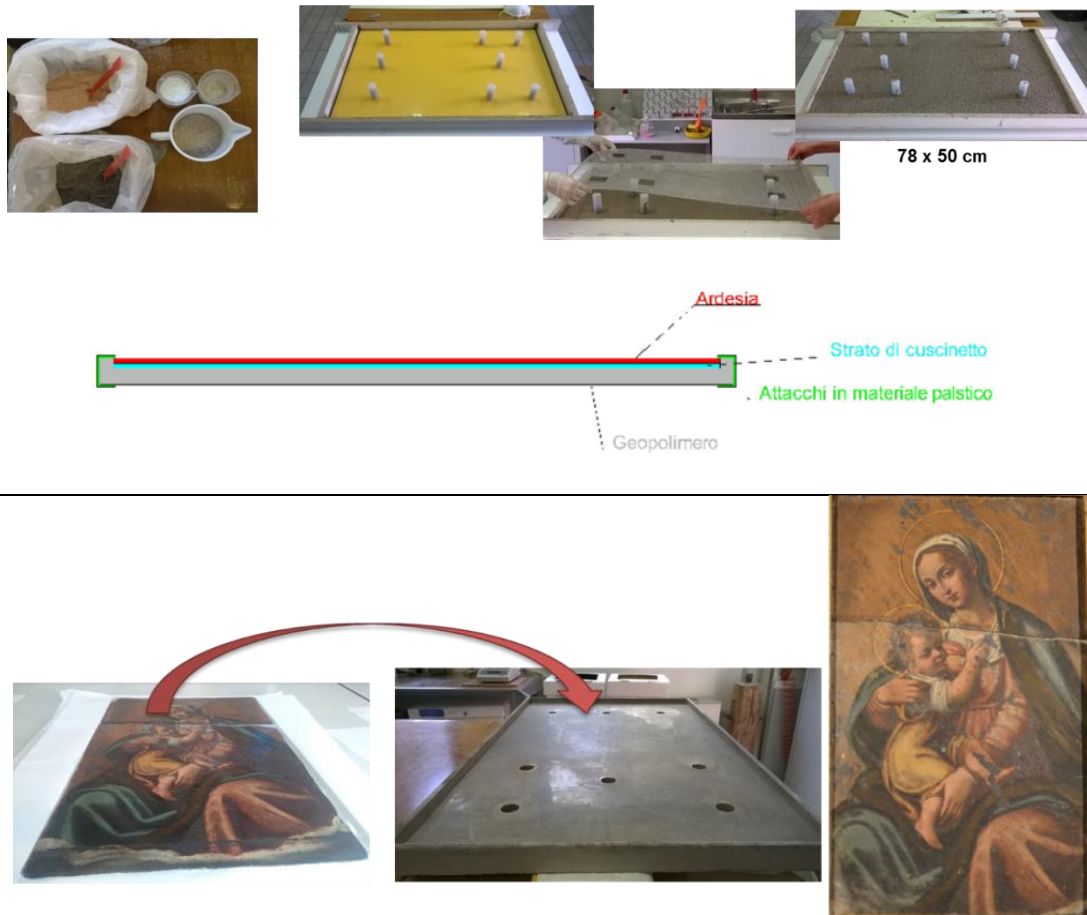
(XVII Century A.D., in Madre di Polizzi Generosa Church, Palermo)

A pre-casted lightweight panel (80x50 cm) was produced in order to contain a slate slab painting. It was obtained by adding slate powder, perlite and polystyrene grains to the geopolymeric binder.

The casting of the material was carried out in two layers to allow the insertion of a reinforcing metal net.

Restorers

G. Salvaggio, G. Inguì, Università di Palermo, Scuola delle Scienze di base e applicate (2015)



5.2

Conservative intervention of a “Roman mosaic fragment”

(I Century A.D, Museo Archeologico, Firenze)

This conservative intervention concerns a Roman floor mosaic in which geopolymer has had a double function.

Part 1: Creation of a geopolymeric container in which the mosaic fragment and the old cement support were completely allocated.

Designed ideas:

two layers different in color for a more controllable reversibility;

lightning to allow vertical position and easier handling;

steel network of structural reinforcement to improve the resistance of the article.

Part 2: Integration of internal and external gaps in the mosaic, placement of tesserae in colorful geopolymer in order to complete the new panel.

The bending and compressing resistances of all these formulation have been tested and the microstructures have been studied using optical and electron microscopy as reported in tables 1-2. From the obtained results the 6D and 6E formulations were chosen.

The samples were produced by laminating two geopolymeric formulations of composite lightened in order to obtain a "sandwich effect" in the interface.

From the “laminated sample” were evaluated:

1. The best color differentiation
2. The lightweight with mechanical performance associated
3. The ability of interpenetration of the two formulations.
4. The interaction of geopolymer with cement, screws, steel network and also the material from formwork and disarming wax.

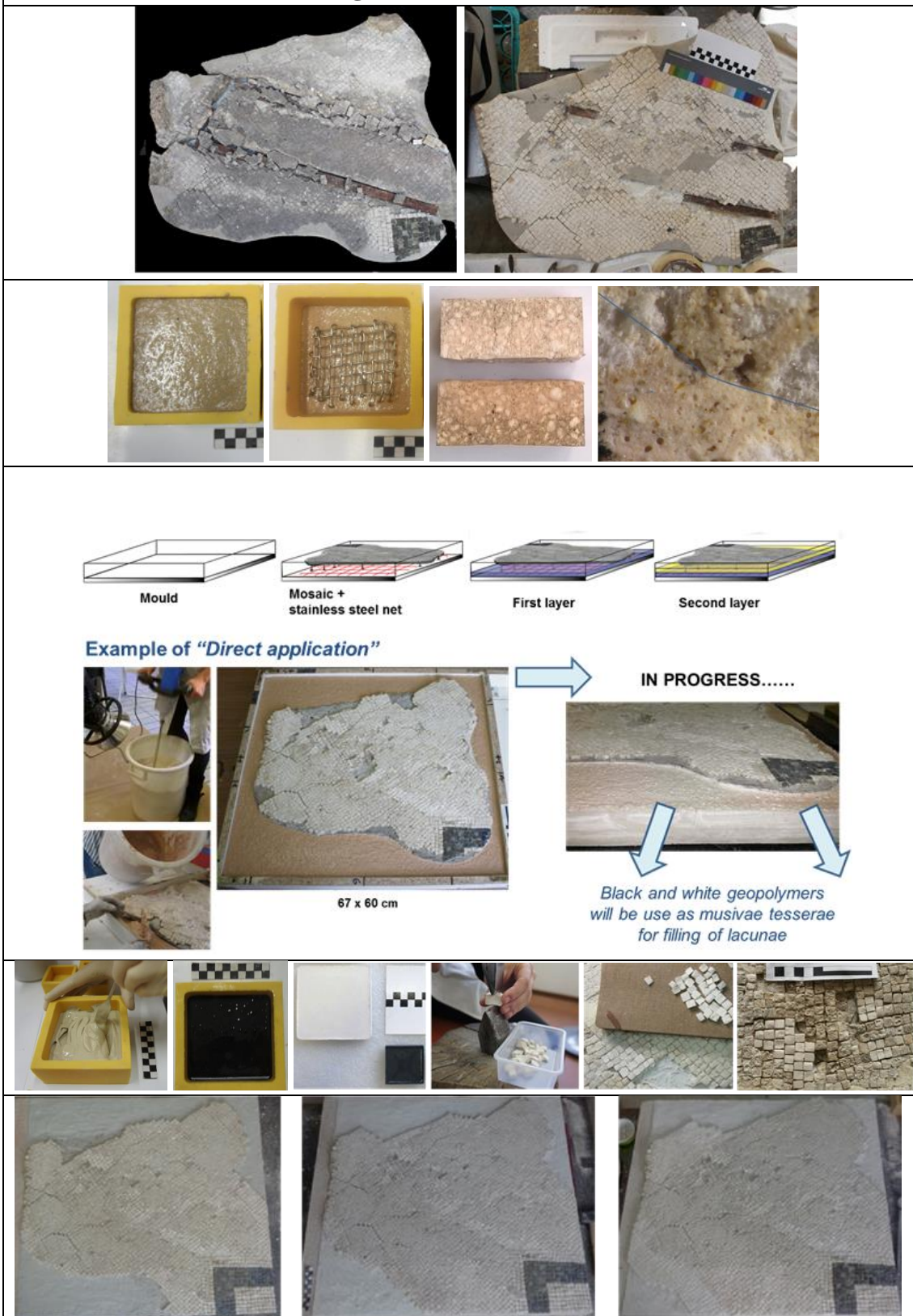
The huge amount of material (about 20 kg) has been mixed in two steps (each one 15 minutes). The mixing and casting of the two layers have been performed with an interval of one hour. Between the first and the second mixture has been inserted (also in this case) a steel net. The panel has been dried to a constant and controlled temperature for about 90 days, and later the superficial part has been integrated.

Integration has been performed over the entire panel's surface with tesserae in white and black geopolymer, different for the material and the color tone. Particular attention has also been given at the form and placement of the tesserae: has been followed the ancient Roman mosaic warp, to obtain a visible but not excessively flat integration.

Restorers:

S. Rindi, Istituto per l'Arte e Restauro Palazzo Spinelli, Firenze

R. Fontanelli, Museo Archeologico, Firenze



5.3

Restoration intervention of a “Sandstone stele”

(I Century A.D, Museo Archeologico, Bologna)

For this intervention the geopolymeric composites were made by using marble powder with mechanical strength comparable with those of natural rock with which they were to interact. Preliminary studies on the strengths of some natural rocks (marble, gneiss, limestone and gypsum) were used to understand the range of the mechanical resistance (Table 3). The composites were mixed and cast as described in Chap 4. The particular shape was chosen for specific purposes. These pivots were inserted into the cuts made in the stele and cemented by means of epoxy resin.

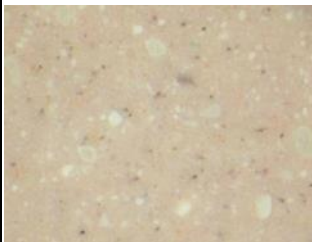
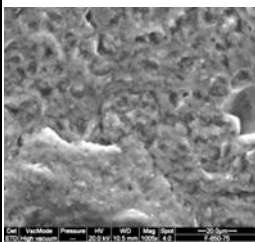
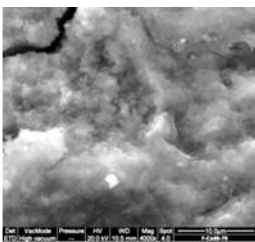
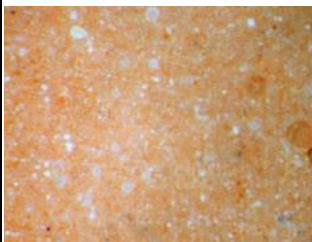
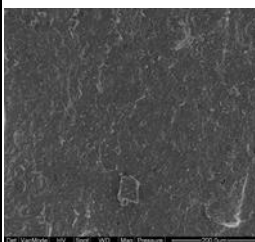
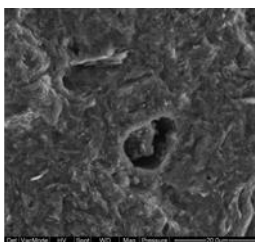
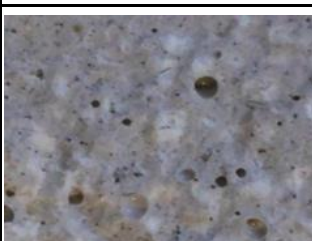
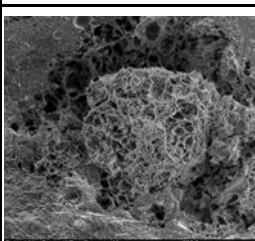
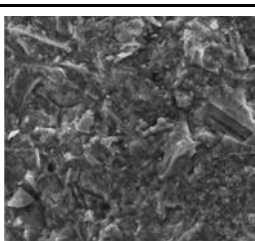
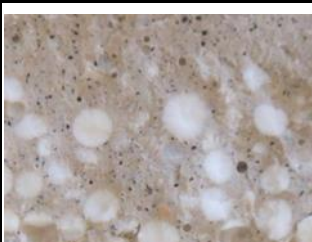
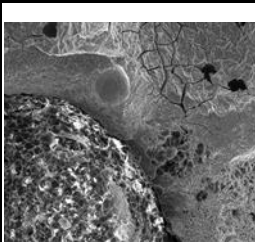
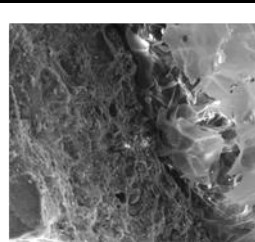
Restorers:

V. Villa, A. Giuffredi, Corso di “Restauro dei materiali lapidei”,
Accademia di Belle Arti di Bologna



Sample	Porosity (%)	Density (g/cm3)	Compression S (MPa)	Flexural S (Mpa)
GEO BS6	40	1,5	51,4 ± 10,0	7,6 ± 4,0
GEO COLOLED	45	1,47 ± 0,02	62,4 ± 12,33	7,4 ± 0,4
GEO 10	-	0,76 ± 0,00	2,51 ± 0,05	0,97 ± 0,13
GEO 9	48	1,22 ± 0,04	24,16 ± 3,61	4,24 ± 0,46
GEO 6D	47	1,18 ± 0,00	12,2 ± 5,8	3,44 ± 2,13
GEO 6E	46	1,20 ± 0,03	15,5 ± 2,9	4,39 ± 0,23
15	22	1,90 ± 0,03	54,77 ± 6,69	9,70 ± 0,81
2A	18,5	2,02 ± 0,02	29,1 ± 5,2	7,50 ± 0,56

Table 1. Mechanical resistance of geopolymeric composites used in these restoration interventions

Sample	Optical microscope	SEM
GEO BS6		 
GEO COLORED		 
GEO 10		 
GEO 9		 

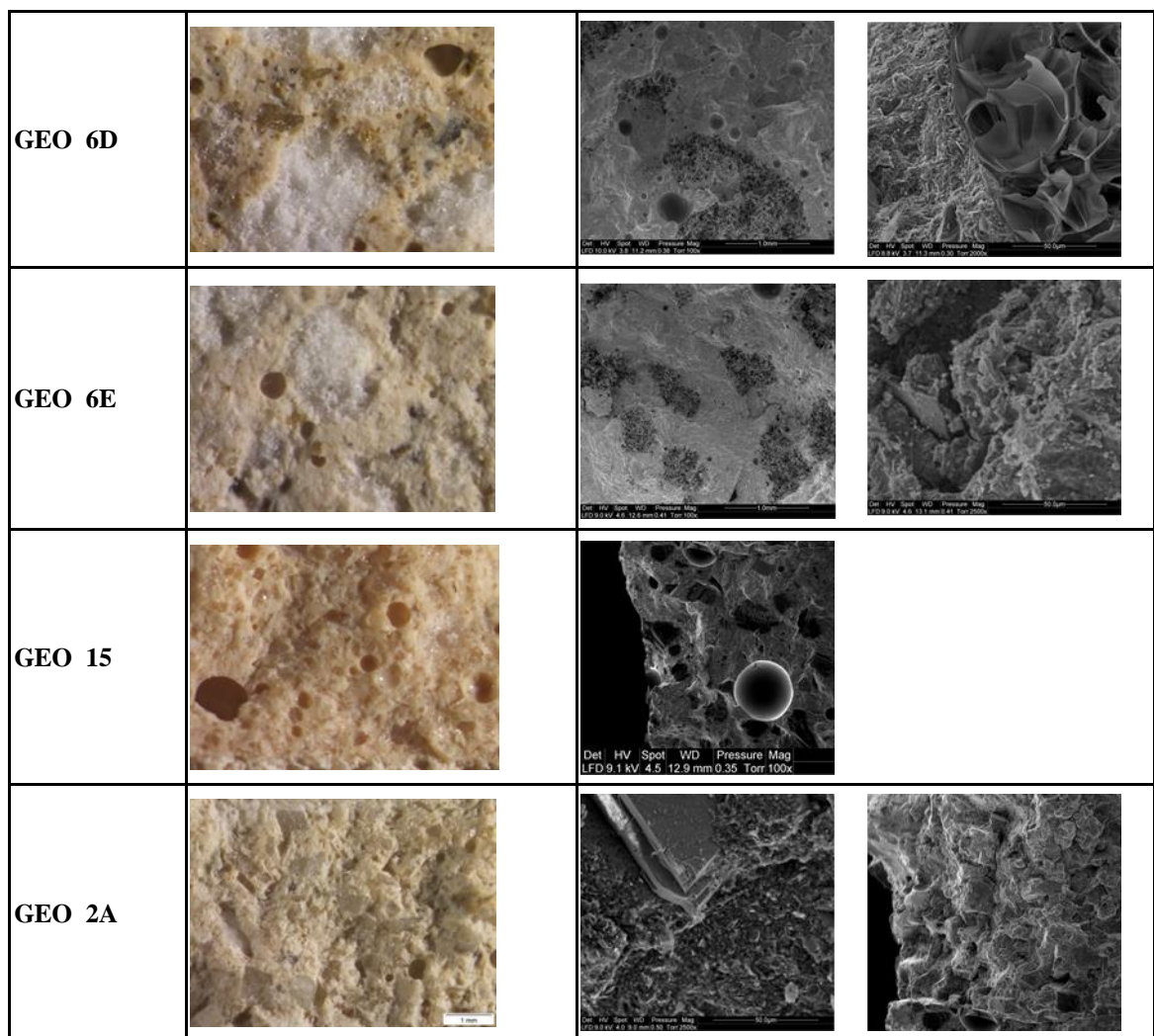


Table 2. Microscopic images of geopolymeric composites used in these restoration interventions


Reference materials	Cmpression S (MPa)	Flexural S (MPa)	
GYPSUM 1	8,17 ± 2,08	3,46 ± 0,45	
GYPSUM 2	8,91 ± 0,64	3,32 ± 0,40	
LIMESTONE	128,05 ± 24,82	19,43 ± 1,05	
MARBLE	45,59 ± 13,45	18,54 ± 0,85	
GNEISS	64,52 ± 20,14	12,72 ± 4,73	

Table 3. Mechanical resistance of reference materials

Chapter 6

Conclusions

For concluding, during these years of activity many formulations have been produced and many of these have been characterized by different analytical techniques, confirming during the time, a good mechanical and chemical stability. Thanks to these results many geopolymeric formulations have been used to produce prototypes. In addition some of these have been applied in real restoration interventions or to produce new artistic objects.

The application part is the result of all the previous experimentation, starting from the characterization of kaolins up to geopolymeric binders and composites.

Of great interest it was to verify that the same kaolin (BS4) treated with two different amorphization processes gave two different metakaolins .

This diversity has been in chemical (reactivity, type of microstructure), physical (porosity, color) and mechanical (less resistance, but with greater homogeneity) properties and it has conditioned the behavior of the final geopolymeric composites.

Equally interesting was to verify that starting from two different kaolins (BS4 and BS6) but using the same treatment of amorphization, it is possible to obtain raw materials with similar properties and similar performances in geopolymers binders and composites.

This experiment opens new doors on both the activation process materials, and on their ability to produce cements alternative to the traditional ones. Geopolymers have been shown to have excellent mechanical properties, they can be added with many fillers and aggregates. They can be colored and can be modified their workability, adapting to the needs of restorers but not only.

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Acknowledgments

I ringraziamenti li farò in italiano, la lingua con cui mi esprimo meglio e quella che viene dal cuore.

Questo lavoro di tesi non sarebbe stato possibile se tante persone non ne avessero fatto parte.

Ringrazio ovviamente l'Università di Bologna, in particolare il mio tutor il Prof. Giuseppe Falini, i professori, i colleghi di corso, ma anche l'ufficio Dottorati.

Un altro grosso ringraziamento va al CNR-ISTEC di Faenza, che mi ha ospitato in questi anni, in particolare alla mia tutor, la Dott.ssa Sabrina Gualtieri, che mi ha seguito quotidianamente. Altri ringraziamenti vanno al Dott. Michele Macchiarola, a tutto il gruppo "Geopolimeri" e a tutto il personale.

Un sentito grazie anche ai tesisti (e relativi tutors) che in questi anni ho potuto aiutare nel loro percorso di tesi e con loro sperimentare: Giuseppe Salvaggio, Laura Samperisi, Simona Rindi, Alessandro Fonti e Veronica Villa.

Un grande grazie anche a Professori, Collaboratori, Restauratori, ecc... che in questi anni hanno fornito "sapere, consigli e strumentazioni".

E poi, per finire, un grossissimo grazie alla mia famiglia e agli amici che mi hanno nuovamente supportata e sopportata nei momenti "no". A loro devo tutto il mio amore e gratitudine.